A COMPREHENSIVE TREATISE
ON
INORGANIC AND THEORETICAL CHEMISTRY

BY

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CONTENTS

	PAGE
ABBREVIATIONS	vii

CHAPTER XVII

THE HALOGENS

§ 1. The Occurrence of Fluorine (1); § 2. The History of Fluorine (3); § 3. The Preparation of Fluorine (7); § 4. The Properties of Fluorine (9); § 5. The Occurrence of Chlorine, Bromine, and Iodine (15); § 6. The History of Chlorine, Bromine, and Iodine (20); § 7. The Preparation of Chlorine (25); § 8. The Preparation of Bromine (38); § 9. The Preparation of Iodine (41); § 10. The Physical Properties of Chlorine, Bromine, and Iodine (46); § 11. Solutions of Chlorine, Bromine, and Iodine in Water, etc. (71); § 12. Chemical Reactions of Chlorine, Bromine, and Iodine (90); § 13. Colloidal Iodine and Iodized Starch (98); § 14. The Atomic Weights of Chlorine, Bromine, and Iodine (101); § 15. The Colour of Solutions of Iodine (110); § 16. Binary Compounds of the Halogens with One Another (118).

CHAPTER XVIII

THE COMPOUNDS OF THE HALOGENS WITH HYDROGEN

§ 1. The Preparation of Hydrogen Fluoride and Hydrofluoric Acid (127); § 2. The Properties of Hydrogen Fluoride and Hydrofluoric Acid (129); § 3. The Fluorides (137); § 4. Equilibrium, and the Kinetic Theory of Chemical Action (141); § 5. The Union of Hydrogen and Chlorine in Light (148); § 6. The Preparation of Hydrogen Chloride and Hydrochloric Acid (158); § 7. The Preparation of Hydrogen Bromide and Hydrobromic Acid (167); § 8. The Preparation of Hydrogen Iodide and Hydriodic Acid (170); § 9. The Physical Properties of the Hydrogen Chloride, Bromide, and Iodide (173); § 10. Properties of Hydrochloric, Hydrobromic, and Hydriodic Acids (182); § 11. The Chemical Properties of the Hydrogen Halides and the Corresponding Acids (200); § 12. The Chlorides, Bromides, and Iodides (214); § 13. Colour Changes on Heating Elements and Compounds (221); § 14. Double and Complex Salts (223); § 15. Double Halides (228); § 16. Perhalides or Polyhalides (233).

CONTENTS

CHAPTER XIX

THE OXIDES AND OXYACIDS OF CHLORINE, BROMINE, AND IODINE

§ 1. Chloride Monoxide (240); § 2. The Preparation of Hypochlorous, Hypobromous, and Hypoiodous Acids (248); § 3. The Properties of the Hypohalous Acids and their Salts (250); § 4. Bleaching Powder (258); § 5. The Hypochlorites, Hypobromites, and Hypoiodites (267); § 6. Electrolytic Processes for the Preparation of Hypochlorites, Hypobromites, and Hypoiodites (276); § 7. Chlorine, Bromine, and Iodine Trioxides; and the Corresponding Acids (281); § 8. Chlorine Di- or Per-oxide (286); § 9. Iodine Di- or Tetra-oxide (291); § 10. The Halogen Pentoxides (293); § 11. The Preparation of Chloric, Bromic, and Iodic Acids, and of their Salts (296); § 12. The Properties of Chloric, Bromic, and Iodic Acids and their Salts (305); § 13. The Halogenates—Chlorates, Bromates, and Iodates—of the Metals (324); § 14. Perchloric Acid and the Perchlorates (370); § 15. Perbromic Acid and the Perbromates (384); § 16. Periodic Acid and the Periodates (386); § 17. The Perchlorates (395); § 18. Periodates (406).

CHAPTER XX

THE ALKALI METALS

§ 1. The History of the Alkali Metals (419); § 2. The Occurrence of the Alkali Metals (423); § 3. The Potash Salt Beds (427); § 4. The Extraction of Potassium Salts (436); § 5. The Extraction of Lithium, Rubidium, and Cæsium Salts (442); § 6. The Preparation of the Alkali Metals (445); § 7. The Properties of the Alkali Metals (451); § 8. The Binary Alloys of the Alkali Metals (478); § 9. The Hydrides of the Alkali Metals (481); § 10. The Oxides of the Alkali Metals (484); § 11. Hydroxides of the Alkali Metals (495); § 12. The Alkali Fluorides (512); § 13. Ammonium Fluoride (519); § 14. The Alkali Chlorides (521); § 15. The Properties of the Alkali Chlorides (529); § 16. Ammonium Chloride (561); § 17. The Alkali Bromides (577); § 18. Ammonium Bromide (590); § 19. The Alkali Iodides (596); § 20. Ammonium Iodide (615); § 21. The Alkali Monosulphides (621); § 22. The Alkali Polysulphides (629); § 23. The Alkali Hydrosulphides (641); § 24. Ammonium Sulphides (645); § 25. The Alkali Sulphates (656); § 26. Alkali Acid Sulphates; Alkali Hydrosulphates (677); § 27. Ammonium Sulphates (694); § 28. The Occurrence and Preparation of the Alkali Carbonates (710); § 29. The Manufacture of Soda by N. Leblanc's Process (728); § 30. The Ammonia-Soda or E. Solvay's Process (737); § 31. The Properties of the Alkali Carbonates (747); § 32. The Alkali Hydrocarbonates, Bicarbonates, or Acid Carbonates (772); § 33. The Ammonium Carbonates (780); § 34. Carbamic Acid and the Carbamates (792); § 35. Commercial "Ammonium Carbonate" (797); § 36. The Alkali Nitrates (802); § 37. Gunpowder (825); § 38. Ammonium Nitrate (829); § 39. Normal or Tertiary Alkali Orthophosphates (847); § 40. Secondary Alkali Orthophosphates (851); § 41. Primary Alkali Orthophosphates (858); § 42. Alkali Pyrophosphates or Diphosphates (862); § 43. Alkali Metaphosphates (867); § 44. Ammonium Phosphates (871); § 45. The Relation between the Alkali Metals (879).

INDEX 881

ABBREVIATIONS

Aq. = aqueous
atm. = atmospheric or atmosphere(s)
at. vol. = atomic volume(s)
at. wt. = atomic weight(s)
T° or °K = absolute degrees of temperature
b.p. = boiling point(s)
°θ = centigrade degrees of temperature
coeff. = coefficient
conc. = concentrated or concentration
dil. = dilute
eq. = equivalent(s)
f.p. = freezing point(s)
m.p. = melting point(s)
mol(s) = {gram-molecule(s) / gram-molecular}
mol(s). = {molecule(s) / molecular}
mol. ht. = molecular heat(s)
mol. vol. = molecular volume(s)
mol. wt. = molecular weight(s)
press. = pressure(s)
sat. = saturated
soln. = solution(s)
sp. gr. = specific gravity (gravities)
sp. ht. = specific heat(s)
sp. vol. = specific volume(s)
temp. = temperature(s)
vap. = vapour

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CHAPTER XVII

THE HALOGENS

§ 1. The Occurrence of Fluorine

THE four elements fluorine, chlorine, bromine, and iodine together form a remarkable family, and they are grouped under the name **halogens** or salt-formers—ἅλς, sea-salt; γεννάω, I produce. J. S. C. Schweigger used this term in 1811, and it was also employed by J. J. Berzelius[1] for the non-oxygenated negative radicles—simple or compound—which combine with the metals to form salts. J. J. Berzelius was inclined to restrict the term more particularly to the simple radicles F, Cl, Br, I, and the compound radicle CN. J. J. Berzelius' term halogen has been retained for the four elements, and cyanogen dropped from the list. The binary salts—fluorides, chlorides, bromides, and iodides—are called **halides,** *halide salts*, or *haloid salts*. This term was also employed by J. J. Berzelius for the salts formed by the union of the metals with fluorine, chlorine, bromine, iodine, and cyanogen; as before, cyanogen has again been dropped from the list.

The first member of the family of halogens, fluorine, is the most chemically active element known; the chemical activity of the other members decreases with increasing at. wt. Fluorine can scarcely be said to occur free in nature, although C. A. Kenngott (1853) and F. Wöhler (1861) suggested that the violet felspar of Wölsendorf, and H. Becquerel and H. Moissan (1890)[2] that the violet fluorspar from Quincié (Villefranche), probably contain free fluorine as an occluded gas. These varieties of fluorspar were designated *hepatischer Flussspath* and *Stinkflussspath* by K. C. von Leonhard (1821) and J. F. L. Hausmann (1847).[3] When these minerals are powdered they emit a peculiar odour recalling ozone, and this has been attributed by various observers to the presence of various substances—*e.g.* hypochlorous acid (M. Schafhäutel), ozone (C. F. Schönbein), free fluorine, or of fluorine from the dissociation of an unstable fluoride or perfluoride (O. Loew).[4] The chemical reactions of the gas, however, were found by H. Becquerel and H. Moissan to correspond with fluorine which must be present either as occluded free fluorine, or else as an unstable perfluoride. The evidence is not decisive though the former is the more probable explanation of the reactions. P. Lebeau[5] obtained similar indications of fluorine in emeralds obtained from the vicinity of Limoges.

Combined fluorine is fairly widely distributed in rocks. According to F. W. Clarke,[6] it is about half as abundant as chlorine, since he estimates that the terrestrial matter in the half-mile crust—land and sea—contains 0·2 per cent. of chlorine, and 0·1 per cent. of fluorine. F. W. Clarke places fluorine the 20th and chlorine the 12th in the list of elements arranged in the order of their estimated abundance in the half-mile crust of the earth. Small quantities of fluorine are commonly present in igneous rocks. J. H. L. Vogt estimated that fluorine is the more abundant in the acidic rocks; chlorine, in the basic rocks. The most characteristic minerals containing fluorine are *fluorspar, fluor*, or *fluorite*—calcium fluoride—and *cryolite*—a double fluoride of aluminium and sodium; the less important or rarer fluoriferous minerals are: *fluellite*, $AlF_3.H_2O$; *chiolite*, $5NaF.3AlF_3$; *sellaite*, MgF_2; *tysonite*, $(Ce, La, Di)F_3$; *pachnolite* and *thomsenolite*, $NaF.CaF_2.AlF_3.H_2O$; *ralstonite*, $2NaF.MgF_2.6Al(F,OH)_3.4H_2O$; *prosopite*, $CaF_2.2Al(F,OH)_3$. Fluorine is also contained in some phosphates—*e.g.* fluorapatite, phosphorite, sombrerite, coprolites,

and staffelite; and in some silicates—*e.g.* topaz, tourmaline, herderite, yttrocerite, amphibole, nocerine, kodolite, melinophane, hieratite, lepidolite, and in many other silicate minerals.

Several mineral waters have been reported to contain minute quantities of soluble fluorides. The spring at Gerez (Portugal) is one of the richest, for, according to C. Lepierre,[7] it contains 0·296 to 0·310 grm. of solid matter per litre, and of this, 0·022 to 0·027 grm. is an alkali fluoride; and of the 93 spring waters examined by P. Carles, 87 contained soluble fluorides. F. Parmentier has denied the existence of fluorine in many waters in which it is supposed to exist; but according to A. Gautier and P. Clausmann, all mineral waters contain fluorine, and the proportion is greatest in waters of volcanic origin. Thermal alkali bicarbonate waters are particularly rich in the element, although the proportion does not appear to depend upon the temp. As a general rule, mineral waters of the same kind show an increase of fluorine accompanying a rise in the total salts. In the case of calcium sulphate waters, whatever their origin, the amount of fluorine is about 2 mgrms. per litre. In 1849, G. Wilson reported on the occurrence of fluorine in the Clyde waters, and in the North Sea; and generally it has been found that sea water contains about three milligrammes per litre; the proportion varies slightly in different places and at different depths. A. Gautier[8] found about 0·11 mgrm. of combined fluorine per litre of gas collected from a fumerole fissure in the crater of Vesuvius; and 3·72 mgrms. per litre in the condensed water from the boric acid fumerole of a spring at Larderello (Tuscany).

At the beginning of the nineteenth century L. J. Proust and M. de la Méthérie[9] first noticed the presence of fluorine in bones, and the fact has since been confirmed by numerous others. A. Carnot found 0·20 to 0·65 per cent. of calcium fluoride in fresh bones, while old fossil bones contained much more—0·88 to 6·21 per cent. This fact was first noticed by J. Stocklasa in 1889. Modern bones were found by A. Carnot to contain a minimum proportion of fluorine; tertiary bones contained more; mesozoic bones still more; and in silurian and devonian bones, the proportion of fluorine was nearly the same as in apatite. A. Carnot attributes the progressive enrichment of bones to the action of percolating waters containing a small proportion of fluorides in soln.—*e.g.* the waters of the Atlantic contain 0·822 grm. per cubic metre. According to F. Hoppe, the enamel of the teeth contains up to 2 per cent. of calcium fluoride; and according to W. Hempel and W. Scheffler, the teeth of horses contain 0·20 to 0·39 per cent. of fluorine, and the teeth of man, 0·33 to 0·59 per cent.[10]—unsound teeth had but 0·19 per cent. of fluorine. P. Carles[11] found 0·012 per cent. of fluorine in the shells of oysters and mussels living in sea water, while fossil oyster shells contained 0·015 per cent. He also reported about one-fourth as much fluorine in fresh-water mussel shells as is present in the shells of sea-water mussels. The brain (E. N. Horsford),[12] blood (G. Wilson, and G. O. Rees), and the milk of animals (F. S. Horstmar) have some fluorine. The brain of man contains about 3 mgrms. of fluorine, and although the *rôle* of fluorine in the animal and vegetable organism has not been clearly defined, some physiologists believe that the presence of fluorine is necessary, in some subtle way, to enable the animal organism to assimilate phosphorus. G. Tammann found that least fluorine was contained in the shells of eggs, and most in the yolks. About 0·1 per cent. of fluorine occurs in the ash of vegetable matter—particularly the grasses.[13] A. G. Woodman and H. P. Talbot reported that fluorine is common in malt liquors; most malted beers contain not less than 0·2 mgrm. per litre. T. L. Phipson has reported 3·9 per cent. of fluorine, and 32·45 of phosphoric acid in fossil wood from the Isle of Wight, thus showing that the wood had been "fossilized by phosphate of lime and fluorspar."

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§ 2. The History of Fluorine

The mineral now known as **fluorspar** or **fluorite** was mentioned in 1529 by G. Agricola, in his *Bermannus, sive de re metallica dialogus* (Basiliæ, 1529), and designated *fluores*, which, in a later work [1] by the same writer, was translated into *Flüsse*. A. J. Cronstedt,[2] in 1758, used the terms *Fluss*, *Flusspat*, and *Glasspat*, synonymously. C. A. Napione (1797) called the mineral *fluorite*; F. S. Beudant (1832), *fluorine*; and M. Sage (1777), *spath fusible*. These terms are derived from the Latin *fluo*, I flow, in reference to the fluxing action and the ready fusibility of the mineral; consequently, *fluor lapis*, *spatum vitreum*, and *Glasspath* mean the fluxing stone. J. G. Wallerius [3] refers to the luminescence of the mineral when warmed, and this phenomenon led to its being called *lithophosphorus* and *phosphoric spar*. The variety which gives a greenish phosphorescence is called *chlorophane*—χλωρός, green; φαίνω, I appear—and also *pyro-emerald*.

H. Kopp reports [4] that H. Schwanhardt in 1670 etched glass by the action of fluorspar and sulphuric acid, and that in 1725, M. Pauli made a liquid for etching glass by mixing nitric acid and powdered fluorspar. In 1764, A. S. Marggraff [5] distilled the mixture of sulphuric acid and fluorspar in a glass retort, and found a white powder to be suspended in the water of the receiver. He therefore concluded that the sulphuric acid separates a volatile earth from the fluorspar. C. W. Scheele [6] repeated A. S. Marggraff's experiment, and, in his *Examen chemicum fluoris mineralis ejusque acidi* (1771), concluded that the sulphuric acid liberates a peculiar acid which is united with lime in fluorspar. The acid was called *Flussäure*—fluor acid—and fluorspar was designated *flusssäurer Kalk*. After the expulsion of the fluor acid from the lime by sulphuric acid, selenite—calcium sulphate—remained in the retort. He found that hydrochloric, nitric, or phosphoric acid could also be used in place of sulphuric acid with analogous results. M. Boullanger [7] took the

view that Scheele's fluor acid was nothing but muriatic acid combined with some earthy substance, and A. G. Monnet that it was a volatile compound of sulphuric acid and fluor. C. W. Scheele,[8] however, refuted both hypotheses in 1780; and concluded:

I hope that I have now demonstrated that the acid of fluor is and remains entirely a mineral acid *sui generis*.

C. W. Scheele generally used glass retorts for the preparation of the acid, and he was much perplexed by the deposit of silica obtained in the receiver. C. W. Scheele thought that the new acid had the property of forming silica when in contact with water, and it was therefore regarded as containing combined silica. The source of the silica was subsequently traced by J. C. F. Meyer and J. C. Wiegleb [9] to the glass of the retorts, and was not formed when the distillation was effected in metal vessels, and the acid vapours dissolved in water contained in leaden vessels. The gas obtained when the fluorspar is treated with sulphuric acid in metal vessels is hydrofluoric acid, and if in glass vessels, some hydrofluosilicic acid is mixed with the hydrofluoric acid.

In Lavoisier's system,[10] Scheele's acid of fluor became *l'acide fluorique*—a combination of oxygen with an unknown radicle, *fluorium*; and in 1789, A. L. Lavoisier wrote:

It remains to-day to determine the nature of the fluoric radicle, but since the acid has not yet been decomposed, we cannot form any conception of the radicle.

In 1809, J. L. Gay Lussac and L. J. Thénard [11] attempted to prepare pure hydrofluoric acid, and although they did not succeed in making the anhydrous acid, they did elucidate the relation of silica and the silicates to this acid. H. Davy's work on the elementary nature of chlorine was published about this time; and he received two letters—dated Nov. 1st, 1810, and Aug. 25th, 1812 [12]—from A. Ampère suggesting "many ingenious and original arguments" in favour of the analogy between hydrochloric and hydrofluoric acids. In the first letter, A. Ampère said:

It remains to be seen whether electricity would not decompose liquid hydrofluoric acid if water were removed as far as possible, hydrogen going to one side and oxyfluoric acid to the other, just as when water and hydromuriatic acid are decomposed by the same agent. The only difficulty to be feared is the combination of the oxyfluoric acid set free with the conductor with which it would be brought into contact in the nascent state. Perhaps there is no metal with which it would not combine, but supposing that oxyfluoric acid should, like oxymuriatic acid, be incapable of combining with carbon, this latter body might be a sufficiently good conductor for it to be used with success as such in this experiment.

In the second letter, A. Ampère suggested that the supposed element be called *le fluor*—*fluorine*—in agreement with the then recently adopted name *chlorine*—French, *le chlore*. A. Ampère's suggestion has been adopted universally. No one doubted the existence of the unknown element fluorine although it successfully resisted every attempt to bring it into the world of known facts. Belief in its existence rested on the many analogies of its compounds with the other three members of the halogen family. For over seventy years it was neither seen nor handled. During this time, many unsuccessful experiments were made to isolate the element. H. Davy [13] thus describes his attempts:

I undertook the experiment of electrizing pure liquid fluoric acid with considerable interest, as it seemed to offer the most probable method of ascertaining its real nature, but considerable difficulties occurred in executing the process. The liquid fluoric acid immediately destroys glass and all animal and vegetable substances, it acts on all bodies containing metallic oxides, and I know of no substances which are not rapidly dissolved or decomposed by it, except metals, charcoal, phosphorus, sulphur, and certain combinations of chlorine. I attempted to make tubes of sulphur, of muriates of lead, and of copper containing metallic wires, by which it might be electrized, but without success. I succeeded,

however, in boring a piece of horn silver in such a manner that I was able to cement a platina wire into it, by means of a spirit lamp, and by inverting this in a tray of platina filled with liquid fluoric acid I contrived to submit the fluid to the agency of electricity in such a manner that in successive experiments it was possible to collect any elastic fluid that might be produced.

Having failed to isolate the element by the electrolysis of hydrofluoric acid and the fluorides, H. Davy tried if the element could be driven from its combination by double decomposition. He attempted to drive the "fluoric principle" from the dry fluates of mercury, silver, potassium, and sodium by means of chlorine. He said:

The dry salts were introduced in small quantities into glass retorts, which were exhausted and then filled with pure chlorine; the part of the retort in contact with the salt was heated gradually till it became red. There was soon a strong action, the fluate of mercury was rapidly converted into corrosive sublimate, and the fluate of silver more slowly became horn silver. In both experiments there was a violent action upon the whole of the interior of the retort. On examining the results, it was found that in both instances there had been a considerable absorption of chlorine, and a production of silicated fluoric acid gas and oxygen gas. I tried similar experiments with similar results upon dry fluate of potassa and soda. By the action of a red-heat they were slowly converted into muriates with the absorption of chlorine, and the production of oxygen, and silicated fluoric acid gas, the retort being corroded even to its neck.

H. Davy assumed that his failure to obtain the unknown element was due to the potency of its reactions. H. Davy tried vessels of sulphur, carbon, gold, horn silver, and platinum, but none appeared to be capable of resisting its action, and "its strong affinities and high decomposing agencies" led to its being regarded as a kind of alcahest or universal solvent. G. Aimé (1833) employed a vessel of caoutchouc, with no better result. The brothers C. J. and T. Knox (1836) [14] sagaciously tried to elude this difficulty by treating silver or mercury fluoride with chlorine in an apparatus made of fluorspar itself. E. Frémy believed that the failure in this as well as in P. Louyet's analogous attempt with fluorspar or cryolite vessels, in 1846, was due to the fact that the two fluorides do not decompose when moisture is rigorously excluded; and, if moisture be present, they form hydrofluoric acid. E. Frémy also did not succeed in decomposing calcium fluoride by means of oxygen, when heated to a high temp. in a platinum tube. E. Frémy electrolyzed fused fluorides —calcium, potassium, and other metal fluorides—in a platinum crucible with a platinum rod as anode. The platinum wire electrode was much corroded, and a gas was evolved which E. Frémy believed to be fluorine because it decomposed water forming hydrofluoric acid, and displaced iodine from iodides. He was able to decompose calcium fluoride at a high temp. by means of chlorine, and particularly when the fluoride is mixed with carbon. E. Frémy, however, made no further progress in isolating the elusive element, although he did show how anhydrous hydrofluoric acid could be prepared.

G. Gore [15] made some experiments on the electrolysis of silver fluoride and on the action of chlorine or bromine on silver fluoride at 15·5° for 38 days, and at 110° for 6 days, in vessels of various kinds—with vessels of carbon, a volatile carbon fluoride was formed. H. Kammerer [16] failed to prepare the gas by the action of iodine on silver fluoride in sealed glass tubes; according to L. Pfaundler, the product of the action is a mixture of silicon fluoride and oxygen. O. Loew heated cerium tetrafluoride, $CeF_4.H_2O$, or the double salt, $3KF.2CeF_4.2H_2O$, and obtained a gas, which he considered to be fluorine, when the tetrafluoride decomposed forming the trifluoride, CeF_3. B. Brauner also obtained a gas resembling chlorine by heating lead tetrafluoride, or double ammonium lead tetrafluoride, or potassium hydrogen lead fluoride, K_3HPbF_8. In the latter case a mixture of potassium fluoride, KF, and lead difluoride, PbF_2, remained. O. Ruff claims to have made a little fluorine by heating the compound $HKPbF_6$. As H. Moissan has said, it is possible that fluorine might be obtained by a chemical process in which a higher fluoride decomposes into a lower fluoride with the liberation of fluorine—say, $2CeF_4=2CeF_3+F_2$. O. Ruff has failed to confirm B. Brauner's observations with the fluorides in question. With lead tetrafluoride in a platinum vessel, lead difluoride and platinum tetrafluoride are formed; liquid or gaseous silicon tetrafluoride is practically without action on the salt although a small quantity of a gas which acts on potassium iodide is formed without altering the

composition of the gas. Antimony pentafluoride acts similarly. With sulphur and iodine the corresponding higher fluorides are formed. Other suggestions have also been made to prepare fluorine by chemical processes. O. T. Christensen[17] proposed heating the higher double fluorides of manganese; A. C. Oudemans, potassium fluorbromate; and H. Moissan, platinum fluophosphates. About 1883, H. B. Dixon and H. B. Baker made an attempt to displace fluorine by oxygen from uranium pentafluoride, UF_5. A. Baudrimont tried the action of boron trifluoride on lead oxide without success. Abortive attempts have been made by L. Varenne, J. P. Prat, P. Cillis, and T. L. Phipson[18] to prepare the gas by wet processes analogous to those employed for chlorine by the oxidation of soln. containing hydrofluoric acid. We now know that this is altogether a wrong line of attack. Some of the dry processes indicated above may have furnished some fluorine; for example, in H. B. Dixon and H. B. Baker's experiment, silver foil in the vicinity of the uranium fluoride was spotted with white silver fluoride; gold foil, with yellow auric fluoride; and platinum foil, with chocolate platinic fluoride.

In 1834, M. Faraday[19] thought that he had obtained fluorine "in a separate state" by electrolyzing fused fluorides, but later, he added:

> I have not obtained fluorine; my expectations, amounting to conviction, passed away one by one when subject to rigorous examination.

This was virtually the position of the fluorine question about 1883, when H. Moissan,[20] a pupil of E. Frémy, commenced systematic work on the subject, and the reports of the various stages of his work have been collected in his important monograph *Le fluor et ses composés* (Paris, 1900). He first tried (1) The decomposition of gaseous fluorides by sparking—*e.g.* the fluorides of silicon, SiF_4; phosphorus, PF_5; boron, BF_3; and arsenic, AsF_3. The silicon and boron fluorides are stable. Phosphorus trifluoride forms the pentafluoride. The fluorine derived from phosphorus pentafluoride reacts with the material of which the vessel is made; similarly with arsenic fluoride. (2) The action of platinum at a red heat on the fluorides of phosphorus and silicon. Phosphorus pentafluoride furnishes some fluorine which unites with the platinum of the apparatus used; phosphorus trifluoride formed the pentafluoride and fluo-phosphides of platinum; silicon tetrafluoride gave no signs of free fluorine; H. Moissan came to the conclusion that no reaction carried out at a high temp. was likely to be fruitful. (3) The electrolysis of arsenic trifluoride to which some potassium hydrogen fluoride was added to make the liquid conducting; any fluoride given off at the anode was absorbed by the electrolyte forming arsenic pentafluoride.

H. Moissan then tried the electrolysis of highly purified anhydrous hydrofluoric acid, but he found, consonant with G. Gore's and M. Faraday's observations,[21] that anhydrous hydrofluoric acid is a non-conductor of electricity. If a small quantity of water be present, this alone is decomposed, and a large quantity of ozone is formed. As the water is broken up, the acid becomes less and less conducting, and, when the whole has disappeared, the anhydrous acid no longer allows a current to pass. He obtained an acid so free from water that "a current of 35 ampères furnished by fifty Bunsen cells was totally stopped." The current passed readily when fragments of dry potassium hydrogen fluoride KF.HF, were dissolved in the acid, and a gaseous product was liberated at each electrode. Success! The element fluorine was isolated by Henri Moissan on June 26th, 1886, during the electrolysis of a soln. of potassium fluoride in anhydrous hydrofluoric acid, in an apparatus made wholly of platinum. In this way, H. Moissan solved what H. E. Roscoe called one of the most difficult problems in modern chemistry.

While the new element possessed special properties which gave it an individuality of its own, and a few surprises occurred during the study of some of its combinations; yet the harmonious analogy between the members of the halogen family—fluorine, chlorine, bromine, and iodine—was fully vindicated. With fluorine in the world of reality, chemists were unanimous in placing the newly discovered element at the head of the halogen family, and in that very position which had been so long assigned to it by presentiment or faith.

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§ 3. The Preparation of Fluorine

When an electric current is passed through a conc. aq. soln. of hydrogen chloride, chlorine is liberated at the anode, and hydrogen at the cathode. When aq. hydrofluoric acid is treated in the same way, water alone is decomposed, for oxygen is liberated at the anode, and hydrogen at the cathode. The anhydrous acid does not conduct electricity, and it cannot therefore be electrolyzed. H. Moissan found that if potassium fluoride be dissolved in the liquid hydrogen fluoride, the soln. readily conducts electricity, and when electrolyzed, hydrogen is evolved at the cathode, and fluorine at the anode. In the first approximation, it is supposed that the primary products of the electrolysis are potassium at the anode, fluorine at the cathode: $2KHF_2=2HF+2K+F_2$. The potassium reacts with the hydrogen fluoride reforming fluoride and liberating hydrogen: $2K+2HF=2KF+H_2$. The reaction is probably more complex than this, and the platinum of the electrodes plays a part in the secondary reactions. Possibly the fluorine first forms platinum fluoride, PtF_4, which produces a double compound with the potassium fluoride.

This compound is considered to be the electrolyte which on decomposition forms the two gases and a double potassium platinum fluoride which is deposited as a black mud. This hypothesis has been devised to explain why the initial stage of the electrolysis is irregular and jerky, and only after the lapse of an hour, when the substances in soln. are in sufficient quantities to make the passage of the current regular, is the evolution of fluorine regular. O. Ruff[1] has shown that ammonium fluoride can be used in place of the potassium salt.

H. Moissan first conducted the electrolysis in a U-tube made from an alloy of platinum and iridium which is less attacked by fluorine than platinum alone. Later experiments

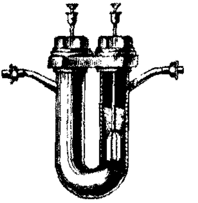

FIG. 1.—Tube for the Electrolysis of Hydrofluoric Acid.

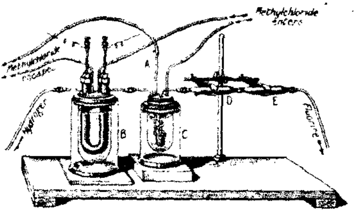

FIG. 2.—Moissan's Process for Fluorine.

showed that a tube of copper could be employed. The copper is attacked by the fluorine, forming a surface crust of copper fluoride which protects the tube from further action. Electrodes of platinum iridium alloy were used at first, but later electrodes of pure platinum were used, even though they were rather more attacked than the alloy with 10 per cent. of iridium. The electrodes were club-shaped at one end so that they need not be renewed so often. The positive electrode was often completely corroded during an experiment, but the U-tube scarcely suffered at all. A copper tube is illustrated in Fig. 1. The open ends of the tube are closed with fluorspar stoppers ground to fit the tubes and bored with holes which grip the electrodes. The joints are made air-tight with lead washers and shellac. The U-tube, during the electrolysis, is surrounded with a glass cylinder, B, into which liquid methyl chloride is passed from a steel cylinder *via* the tube A, Fig. 2. Liquid methyl chloride boils at $-23°$, and it escapes through an exit tube. The fluorine is passed through a spiral platinum tube also placed in a bath of evaporating liquid methyl chloride, C. This cools the spiral tube down to about $-50°$, and condenses any gaseous hydrogen fluoride, which might escape with the fluorine from the U-tube. The electrolysis was carried out at a low temp. in order to prevent the gaseous product being dil. with the vapour of hydrogen fluoride, and also to diminish the destructive action of the fluorine on the apparatus. In his later work, H. Moissan cooled the U-tube used for the electrolysis by using a bath of acetone with solid carbon dioxide in suspension. This cooled the apparatus down to about $-80°$. The temp. of the electrolysis vessel should not be so low that the potassium hydrogen fluoride crystallizes out. Hence, O. Ruff and P. Ipsen[2] preferred to cool the electrolysis vessel with a freezing mixture of calcium chloride, and condensed the hydrogen fluoride vapours in a copper condenser C, Fig. 2, cooled with liquid air. The fluorine which leaves the condenser C, travels through two small platinum tubes, D and E, containing lumps of sodium fluoride, which remove the least traces of hydrogen fluoride by forming NaF.HF. A glass cylinder is placed outside each of the two cylinders containing methyl chloride. The outer cylinders contain a few lumps of calcium chloride, so as to dry the air in the vicinity of the cold jacket, and prevent the

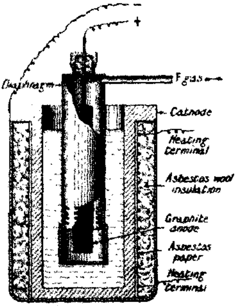

FIG. 3.—Fluorine by the Electrolysis of Fused Alkali Hydrofluoride.

deposition of frost on the cylinders. With a current from 26 to 28 Bunsen cells in series, and an apparatus containing from 90 to 100 grms. of anhydrous hydrofluoric acid containing in soln. 20 to 25 grms. of potassium hydrogen fluoride, H. Moissan obtained between two and three litres of fluorine per hour.

C. Poulenc and M. Meslans[3] have devised a copper apparatus for the preparation of fluorine on a large scale; and likewise a portable laboratory apparatus, also of copper. They substitute a perforated copper diaphragm in place of the *U*-tube for keeping the two electrode products separate. The platinum anode is hollow, and is cooled internally. G. Gallo did not get good results with this apparatus. W. L. Argo and co-workers prepared fluorine by the electrolysis of molten potassium hydrofluoride in an electrically heated copper vessel which served as cathode, the anode being made of graphite. A copper diaphragm with slots was used as illustrated in Fig. 3. The bubbles of hydrogen evolved during the electrolysis were deflected from the interior of the diaphragm by means of a false bottom. The graphite anode was connected with a copper terminal and insulated by a packing of powdered fluorspar —current, 10 amps., 15 volts; temp., 240°–250°; efficiency, 70 per cent. These co-workers also recommend sodium hydrofluoride because it is non-deliquescent; decomposes below the fusion temp.; contains more available fluorine for a given weight; and is less expensive.

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§ 4. The Properties of Fluorine

Is fluorine an element? Since fluorine had never been previously isolated, it remained for H. Moissan to prove that the gas he found to be liberated at the positive pole is really fluorine. Many of its physical and chemical properties, as will be shown later, agree with those suggested by the analogy of the fluorides with the chlorides, bromide, and iodides. It was found impossible to account for its properties by assuming it to be some other gas mixed with nitric acid, chlorine, or ozone; or that it is a hydrogen fluoride richer in fluorine than the normal hydrogen fluoride.

To show the absence of hydrogen, H. Moissan allowed the gas to pass directly from the positive pole through a tube containing red-hot iron; any hydrogen so formed was collected in an atm. of carbon dioxide. The latter was removed by absorption in potassium hydroxide. In several experiments a small bubble of gas was obtained which was air, not hydrogen. The increase in weight of the tube containing the iron corresponded exactly with the fluorine eq. of the hydrogen collected at the negative pole. The vapours of hydrogen fluoride were retained by a tube filled with dry potassium fluoride. For example: In one experiment a platinum tube containing iron increased in weight 0·138 grm. while 80·01 c.c. of hydrogen were collected at the negative electrode. This represents 0·00712 grm. of hydrogen, and $0{\cdot}00712 \times 19 = 0{\cdot}134$ grm. of fluorine. This number is virtually the same as the weight of fluorine actually weighed.

Fluorine at ordinary temp. is a greenish-yellow gas when viewed in layers a metre thick; the colour is paler and more yellow than that of chlorine. The liquid gas is canary-yellow; the solid is pale yellow or white. Moissan's gas has an intensely irritating smell said to recall the odour of hypochlorous acid or of nitrogen peroxide. Even a small trace of gas in the atm. acts quickly on the eyes and the mucous membranes; and, in contact with the skin, it causes severe burns, and rapidly destroys the tissues. If but a slight amount is present, its smell is not

unpleasant. The **relative density** [1] of the gas (air unity) determined by H. Moissan in 1889, by means of a platinum flask, was 1·26; that calculated for a diatomic gas of at. wt. 19·5 is 1·314, and B. Brauner attributed the difference to the presence of some atomic fluorine. H. Moissan's later results (1904) rendered B. Brauner's hypothesis unnecessary since a density of 1·31 was obtained. The gas employed previously is supposed to have been contaminated with a little hydrogen fluoride. Most of the physical properties of fluorine at a low temp. have been determined by H. Moissan himself and in conjunction with J. Dewar.[2] The sp. gr. of liquid fluorine is 1·14 at −200°, and 1·108 at its b.p. −187°. The sp. vol. of the liquid is 0·9025; and the mol. vol. 34·30. The **capillary constant** of the liquid is about one-sixth of that of liquid oxygen, and seven-tenths of that of water. The **coefficient of expansion** [3] of the gas is 0·000304. The volume of the liquid changes one-fourteenth in cooling from −187° to −210°. When the gas is cooled by rapidly boiling liquid air, it condenses to a clear yellow liquid which has the **boiling point** −187° at 760 mm. press.; and the liquid forms a pale yellow solid when cooled by liquid hydrogen. The solid has the **melting point** −233°. The solid loses its yellow tint and becomes white when cooled down to −252°. Chlorine, bromine, sulphur, etc., likewise lose their colour at low temp.

J. H. Gladstone's [4] estimate for the **atomic refraction** of fluorine for the D-line is 0·53; for the A-line 0·63; and for the H-line 0·35 with the μ-formula, and 0·92 and 0·84 respectively with the μ^2-formula. F. Swarts estimated 0·94 H_α, 1·015 D, and 0·963 H_γ with the μ^2-formula for fluorine in sat. organic compounds; and for unsaturated compounds with the ethylene linkage, H_α 0·588; D, 0·665; H_γ, 0·638. The **atomic dispersion** is 0·022 with sat. and 0·05 with the unsaturated compounds. J. H. Gladstone also made several estimates of the index of refraction of fluorine, and his 1870 estimate gave 1·4 (chlorine 9·9); in 1885 he placed it at 1·6; and in 1891, he considered it to be "extremely small, in fact, less than 1·0." The difficulty is due to the fact that when the magnitude of a small constant is estimated by subtraction from two large numbers the probability of error is large. A direct determination by C. Cuthbertson and E. B. R. Prideaux gave for the **index of refraction** of fluorine for sodium light, $\mu=1·000195$, which makes the refractivity $(\mu-1)\times10^6$ to be 195. The **emission spectrum** of fluorine has been investigated by H. Moissan and G. Salet.[5] The last named, in 1873, compared the spectra of silicon chloride and fluoride, and inferred that five lines in the spectrum of silicon fluoride must be attributed to the fluorine. H. Moissan's measurements, in 1889, measured 13 lines in the red part of the spectrum. The lines of wave-length 677, 640·5, 634, and 623 are strong; the lines 714, 704, 691, 687·5, 685·5, 683·5 are faint; and 749, 740, and 734 are very faint. Liquid fluorine has no absorption spectrum when in layers 1 cm. thick.

According to P. Pascal,[6] fluorine is diamagnetic; the specific **magnetic susceptibility** is $-3·447\times10^{-7}$; and the atomic susceptibility calculated from the additive law of mixtures for organic compounds is -63×10^{-1}. Ionic fluorine is univalent and negative. The **decomposition voltage** required to separate this element from its compounds is 1·75 volts.[7] The ionic velocity (transport number) [8] of fluorine ions at 18° is 46·6, and 52·5 at 25° with a temp. coeff. of 0·0238.

Fluorine possesses special characters which place it at the head of the halogen family. It forms certain combinations and enters into some reactions in a way which would not be expected if the properties of the element were predicted solely by analogy with the other members of the halogen family. From this point of view, said H. Moissan, *l'étude des composés fluorés réserve encore bien des surprises*. Fluorine is the most chemically active element known. It combines additively with most of the elements, and it usually behaves like a univalent element although it is very prone to form double or complex compounds in which it probably exerts a higher valency. It also acts as an oxidizing agent. In the electrolysis of manganese and chromium salts a higher yield of chromic acid or manganic acid is obtained in the presence of hydrofluoric acid than in the presence of sulphuric acid.[9] Fluorine

unites explosively with **hydrogen** in the dark with the production of a flame with a red border, and H. Moissan showed this by inverting a jar of hydrogen over the fluorine delivery tube of his apparatus. The product of the action is hydrogen fluoride which rapidly attacks the glass vessel when moisture is present, but not if the two gases are dry. Fluorine retains its great avidity for hydrogen even at temp. as low as $-252.5°$ when the fluorine is solid, and the hydrogen is liquid. H. Moissan and J. Dewar[10] broke a tube of solid fluorine in liquid hydrogen. A violent explosion occurred which shattered to powder the glass apparatus in which the experiment was performed. It is rather unusual for the chemical activity of an element to persist at such a low temp. The affinity of fluorine for hydrogen is so great that it vigorously attacks organic substances, particularly those rich in hydrogen. The reaction is usually accompanied by the evolution of heat and light, and the total destruction of the compound. The products of the reaction are hydrogen fluoride, carbon, and carbon fluorides. The avidity of fluorine for hydrogen persists at very low temp., for turpentine and anthracene may explode in contact with fluorine at $-210°$. *Even* **water** *is vigorously attacked by fluorine.* If a small quantity of water is introduced into a tube containing fluorine, it is decomposed, forming hydrogen fluoride and ozone; the latter imparts an indigo-blue tinge to the gases in the jar. By measuring the volume of oxygen liberated when fluorine reacts with water, and measuring the exact quantity of hydrofluoric acid formed, H. Moissan showed that equal volumes of hydrogen and fluorine form hydrogen fluoride. If the reaction between fluorine and water be symbolized, $H_2O+F_2=2HF+O$, it follows that for every volume of hydrogen collected at the negative pole, half a volume of oxygen should be obtained. In one experiment H. Moissan collected 26·10 c.c. of oxygen, 52·80 c.c. of hydrogen. In another experiment he obtained 6·4 c.c. of oxygen per 12·5 c.c. of hydrogen and eq. of 24·9 c.c. of hydrogen fluoride. Liquid fluorine does not react with water. At $-200°$, liquid fluorine can be volatilized from the surface of ice without reaction.

Neither **oxygen** nor **ozone** appears to react with fluorine, and no oxygen compound of fluorine has yet been prepared. According to H. Moissan,[11] an unstable intermediate compound of ozone and fluorine is possibly formed when water acts on fluorine to form ozonized oxygen because the ozone smell does not appear until some time after the fluorine has been passed into the water. O. Ruff and J. Zedner have tried the effect of heating oxygen and fluorine in the electric arc, but obtained no signs of the formation of a compound of fluorine with oxygen or ozone, for when the gaseous product is passed over calcium chloride (which fixes the fluorine) a mixture is obtained quite free from fluorine. G. Gallo obtained signs of a very unstable compound of ozone and fluorine which is explosive at $-23°$. Liquid oxygen dissolves fluorine, and if the temp. rises gradually, the first fraction which volatilizes is almost pure oxygen; the last fraction contains most of the fluorine. If liquid air, which has stood by itself for some time, be treated with fluorine, a precipitate is formed which is very liable to explode. H. Moissan thinks it is probably *fluorine hydrate.*[12]

Solid **sulphur, selenium,** and **tellurium** inflame in fluorine gas at ordinary temp.; sulphur burns to the hexafluoride, SF_6. The reactivity of sulphur or selenium with fluorine persists at $-187°$, but tellurium is without action at this temp. **Hydrogen sulphide** and **sulphur dioxide** also burn in the gas—the former produces hydrogen fluoride and sulphur fluoride. Each bubble of sulphur dioxide led into a jar of fluorine produces an explosion and thionyl fluoride, SOF_2, is formed; but if the fluorine be led into the sulphur dioxide, there is no action until the sulphur dioxide has reached a certain partial pressure when all explodes. If the fluorine be led into an atm. of sulphur dioxide at the temp. of the reaction, sulphuryl fluoride, SO_2F_2, is formed quietly without violence. **Sulphuric acid** is scarcely affected by fluorine.

Fluorine does not unite with **chlorine** at ordinary temp. O. Ruff and J. Zedner also obtained no result by heating fluorine and chlorine at the temp. of the electric

arc. Liquid chlorine dissolves fluorine, but the dissolved gas escapes as the chlorine freezes. It is inferred that the gases do not react at the low temp. $-80°$ when fluorine is dissolved in liquid chlorine because (i) the gases evolved when the soln. is *fractionally distilled showed no signs of an abrupt change in composition* between 97·32 *per cent. of fluorine at the beginning* and 0·63 per cent. at the end of the operation; (ii) on cooling a soln. of fluorine in liquid chlorine, there is a tumultuous evolution of gas when the mixture freezes the solid is chlorine, the gas fluorine. **Bromine** unites with fluorine at ordinary temp. with a luminous flame forming bromine trifluoride, BrF_3. Similar remarks apply to **iodine**, where the pentafluoride, IF_5, is formed. The heat of the former reaction is small, the latter great. *Liquid fluorine, however, does not react with or dissolve bromine or iodine at* $-187°$, *nor does it liberate iodine from* potassium iodide. In the presence of water, chlorine reacts with fluorine forming hypochlorous acid; and bromine, hypobromous acid; some chloric or bromic acid may also be formed, and part of the water is also decomposed by the excess of fluorine. If fluorine be passed into a 50 per cent. soln. of **hydrofluoric acid**, there is an energetic reaction accompanied by a flame in the midst of the liquid. The reaction of fluorine with gaseous or aq. soln. of **hydrogen chloride, bromide**, or **iodide**, is *accompanied by flame. Most of the haloids of the metalloids are attacked with great energy by fluorine at ordinary temp.*

Fluorine does not unite with argon even if a mixture of the two gases be heated or sparked. Neither **nitrogen** or **nitrous oxide**, N_2O, nor **nitrogen peroxide**, NO_2, is attacked by fluorine at ordinary temp. O. Ruff and J. Zedner also found no reaction occurred at the temp. of the electric arc between fluorine and nitrogen. *Even at a dull red heat* nitrous *oxide remains unattacked by fluorine*, but by sparking a mixture of fluorine and nitrous oxide, a mixture of nitrous oxide, nitrogen, and *oxygen is formed*, but *no nitrogen oxyfluoride*.[13] A little **nitric oxide**, NO, unites with fluorine at ordinary temp.; the reaction is attended by a pale yellow flame, and a volatile oxyfluoride is formed; but if the nitric oxide be in large excess, it is simply broken down into nitrogen and oxygen, and the excess of nitric oxide forms nitrogen peroxide. According to H. Moissan and P. Lebeau, if the fluorine be in excess, at the temp. of liquid oxygen, a white solid is formed which, as the temp. rises, changes into a colourless liquid, boiling above $80°$, and which *furnishes on fractionation nitroxyl or nitryl fluoride*, NO_2F. *Fluorine* decomposes **ammonia** with inflammation; and a mixture of the two gases explodes. **Phosphorus** inflames in fluorine gas forming the pentafluoride, PF_5, if the fluorine be in excess; and the trifluoride, PF_3, if the phosphorus be in excess. **Arsenic** forms the trifluoride, AsF_3, with inflammation. Similarly with antimony; but bismuth is only superficially attacked. Both phosphorus and arsenic react with incandescence with liquid fluorine, but antimony remains unaltered. **Phosphorus pentoxide**, P_2O_5, *is decomposed at a red heat forming the fluoride and oxyfluoride*; **phosphorus tri- and penta-chloride** are attacked with the production of flame; neither **phosphorus pentafluoride** nor **phosphorus oxyfluoride** is attacked. **Arsenic trioxide** and **arsenic trichloride** are attacked. **Arsenic trifluoride**, AsF_3, absorbs fluorine, and the heat generated during the absorption led H. Moissan to suggest that some unstable *arsenic pentafluoride* is formed.

Both **boron** and **silicon** unite with fluorine gas energetically and with incandescence, forming in the one case boron trifluoride, BF_3, and in the other, silicon tetrafluoride, SiF_4. **Boric oxide** and **silica** react energetically in the cold. **Boron trichloride**, BCl_3, at ordinary temp., and **silicon tetrachloride**, $SiCl_4$, above $40°$, both react with fluorine. Dry fluorine does not attack **glass**, for H. Moissan kept dry fluorine in glass vessels for two hours at $100°$, without appreciable attack. Hydrogen fluoride behaves similarly. The slightest trace of moisture is sufficient to activate either gas. Dry lampblack becomes incandescent in fluorine; wood charcoal fires spontaneously; the vigour of the reaction is reduced at low temp., *for boron, silicon, and carbon are not attacked by liquid fluorine.* If powdered charcoal or soot be allowed to fall into a vessel containing liquid fluorine, the particles

become incandescent as they drop through the vapour, but the glow is quenched when the particles reach the liquid. The denser forms of **carbon** require a temp. of 50° to 100° before they become incandescent; retort carbon requires a red heat; and the diamond is not affected at that temp. Soft charcoal is quickly ignited in contact with the gas. The product of the reaction is usually a mixture of different carbon fluorides, but if the temp. of the reaction be kept low, carbon tetrafluoride alone is formed. H. Moissan [14] also found that fluorine acts on **calcium carbide** at ordinary temp. giving calcium fluoride and carbon tetrafluoride. **Carbon monoxide and dioxide** are not attacked in the cold; **carbon disulphide,** CS_2, *inflames forming* carbon and sulphur fluorides; **carbon tetrachloride,** CCl_4, reacts at temp. exceeding 30° forming chlorine and carbon tetrafluoride; **cyanogen** is decomposed at ordinary temp. with the production of a white flame. According to W. L. Argo and co-workers, the unlighted gas issuing from a Bunsen's burner is immediately ignited by fluorine. According to B. Humiston, **acetone** in an open vessel takes fire; **chloroform** forms chlorine, phosgene, and carbon fluorides. With phosgene, a compound which appears to be carbonyl fluoride, COF_2, was formed. The action of fluorine on **ethylene tetrachloride,** C_2Cl_4, is symbolized: $C_2Cl_4+2F_2=C_2F_4+2Cl_2$, followed by $Cl_2+C_2Cl_4=C_2Cl_6$, and $C_2F_4=CF_4+C$.

The **metals** are in general attacked by fluorine at ordinary temp.; many of them become coated with a layer of fluoride which protects them from further action. These remarks apply to the metals: aluminium, bismuth, chromium, copper, gold, iridium, iron, manganese, palladium, platinum, ruthenium, silver, tin, zinc. The formation of a protective skin of fluoride renders it possible to prepare fluorine in copper and platinum vessels at ordinary temp. Lead is slowly converted into the white fluoride at ordinary temp. If the temp. be raised, nearly all the metals are vigorously attacked with incandescence—for example, with tin and zinc, the ignition temp. is about 100°, and iron and silver, at about 500°. Gold and platinum are slowly converted into their fluorides at about 500° or 600°. The metals of the alkalies and alkaline earths, thallium, and magnesium are converted with incandescence into their fluorides. Many of the metals which in bulk are only attacked slowly, are rapidly converted into fluorides if they are in a finely divided condition. Thus fluorine forms a volatile fluoride with powdered molybdenum in the cold, *but a lump of the metal is not attacked; tungsten is attacked at ordinary temp.,* and also forms a volatile fluoride; electrolytic uranium, in fine powder, is vigorously attacked and burns, forming a green volatile hexafluoride. If niobium (columbium) or tantalum be warmed, the pentafluorides are formed. Liquid fluorine has no action on many of the metals—*e.g.* iron. If mercury be quite still, a protecting layer of fluoride is formed, but if the metal be agitated with the gas, it is rapidly converted into the fluoride.

The **chlorides, bromides, iodides,** and **cyanides** are generally vigorously attacked by fluorine in the cold; **sulphides, nitrides,** and **phosphides** are attacked in the cold or may be when warmed a little; the **oxides** of the alkalies and alkaline earths are vigorously attacked with incandescence; the other oxides usually require to be warmed. The **sulphates** usually require warming; the **nitrates** generally resist attack even when warmed. The **phosphates** are more easily attacked than the sulphates. The **carbonates** of sodium, lithium, calcium, and lead are decomposed at ordinary temp. with incandescence, but potassium carbonate is not decomposed even at a dull red heat. Fluorine does not act on sodium **borate.** Most of these reactions have been qualitatively studied by H. Moissan,[15] and described in his monograph, *Le fluor et ses composés* (Paris, 1900).

Atomic and molecular weight of fluorine.—The combining weight of fluorine has been established by converting calcium fluoride, potassium fluoride, sodium fluoride, etc., into the corresponding sulphates. In illustration, J. B. A. Dumas (1860) found that one gram of pure potassium fluoride furnishes 1·4991 gram of potassium sulphate. Given the combining weights of potassium 39·1, sulphur 32·07, oxygen 16, it follows that if x denotes the combining weight of fluorine with

39·1 grams of potassium, 1 : 1·4991=2KF : K_2SO_4=2(39·1+x) : 174·27 ; or, x=19.

H. Davy[10] made the first attempt in this direction in 1814 by converting fluorspar into the corresponding sulphate. His result corresponds with an at. wt. 18·81. J. J. Berzelius (1826) also employed a similar process and obtained first the value 19·16 and later 18·85. P. Louvet, in 1849, employed the same process, taking care that the particles of fluorspar did not escape the action of the sulphuric acid by the formation of a protective coating of sulphate. P. Louvet obtained 18·99 with native fluorspar, and 19·03 with an artificial calcium fluoride. In 1860, J. B. A. Dumas obtained the value 18·95 with calcium fluoride ; S. de Luca (1860), 18·97 ; H. Moissan (1890), 19·011. P. Louvet, J. B. A. Dumas, and H. Moissan also converted sodium fluoride into sodium sulphate and obtained respectively the values 19·06, 19·08, and 19·07. P. Louvet and H. Moissan in addition converted barium fluoride into the sulphate and obtained respectively 19·01 and 19·02 ; and P. Louvet's value, 19·14, was obtained with lead fluoride. O. T. Christensen (1886) treated ammonium manganese fluoride, $(NH_4)_2MnF_5$, with a mixture of potassium iodide and hydrochloric acid—one mol. of the salt gives a gram-atom of iodine. The liberated iodine was titrated with sodium thiosulphate. The value 19·038 was obtained. J. Meyer (1903) converted calcium oxide into fluoride and obtained 19·035. D. J. McAdam and E. F. Smith (1912) obtained 19·015 by transforming sodium fluoride into the chloride. E. F. Smith and W. K. van Haagen obtained 19·005 by converting anhydrous borax into sodium fluoride. E. Moles and T. Batuecas estimated the at. wt. of fluorine from the density of methyl fluoride, and found 18·998±0·005 when the at. wt. of carbon is 12·000, and of hydrogen, 1·0077. The best determinations range between 18·97 and 19·14, and the best representative value of the combining weight of fluorine is taken to be **19**. No known volatile compound of fluorine contains less than 19 parts of fluorine per molecule, and accordingly this same number is taken to represent the at. wt. The vapour density of fluorine, determined by H. Moissan, is 1·31 (air=1), that is, 28·755 ×1·31=37·7(H_2=2). The molecule of fluorine is therefore represented by F_2.

Fluorine is assumed to be univalent since it forms fluorides like KF, NaF, etc. with univalent elements and radicles ; CaF_2, BaF_2, etc., with bivalent radicles, etc. As indicated in connection with hydrogen fluoride, etc., there is, however, the great probability that fluorine also exhibits a higher valency in the more complex compounds like KF.HF, $AlF_3.3NaF$, etc.[17] This also agrees with J. Thomsen's observations on the heat of the reaction between the acid and silica.

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§ 5. The Occurrence of Chlorine, Bromine, and Iodine

Chlorine.—Chlorine does not occur free in nature, but hydrogen chloride has been reported in the fumes from the fumeroles of volcanic districts,[1] Vesuvius, Hecla, etc. D. Franco reported that the gases given off by the flowing lava of Vesuvius, during solidification, contained much hydrogen chloride, and the same gas has been found as an inclusion in minerals. Hydrogen chloride is also found in the springs and rivers of volcanic districts—*e.g.* the Devil's Inkpot (Yellowstone National Park), Paramo de Ruiz (Colombia), Brook Sungi Pait (Java), the Rio Vinagre (Mexico), etc. The latter is said to contain 0·091 per cent. of free hydrochloric acid which is estimated to be eq. to 42,150 kgrms. of HCl per diem.[2] J. B. J. D. Boussingault supposes this acid to be derived from the decomposition of sodium chloride by steam.

Combined chlorine is an essential constituent of many minerals—there are *sal ammoniac* (ammonium chloride); *sylvine* (potassium chloride); *halite* (sodium chloride); *chlorocalcite*, $CaCl_2$; *cerargyrite* or *horn silver*, AgCl; *calomel*, HgCl; *terlinguaite*, Hg_2OCl; *eglestonite*, Hg_4Cl_2O; *molysite*, $FeCl_3$; *erythrosiderite*, $2KCl.FeCl_3.H_2O$; *rinneite*, $3KCl.NaCl.FeCl_2$; *kremersite*, $2KCl.2NH_4Cl.2FeCl_3.3H_2O$; *lawrencite*, $FeCl_2$; *douglasite*, $2KCl.FeCl_2.2H_2O$; *scacchite*, $MnCl_2$; *cotunnite*, $PbCl_2$; *matlockite*, $PbCl_2.PbO$; *penfieldite*, $2PbCl_2.PbO$; *mendipite*, $PbCl_2.2PbO$; *laurionite*, $PbCl_2.Pb(OH)_2$; *fiedlerite*, $2PbCl_2.Pb(OH)_2$; *rafaelite* or *paralaurionite*, PbCl(OH); *nantokite*, CuCl; *melanothallite*, $CuCl_2.CuO.H_2O$; *hydromelanothallite*, $CuCl_2.CuO.2H_2O$; *atacamite*, $Cu_2Cl(OH)_3$; *percylite*, $PbCuCl(OH)_2$; *boleite*, $3PbCuCl_2(OH)_2.AgCl$; *footeite*, $CuCl_2.8Cu(OH)_2.4H_2O$; *tallingite*, $CuCl_2.4Cu(OH)_2.4H_2O$; *atelite*, $CuCl_2.2Cu(OH)_2.H_2O$; *cumengeite*, $4PbCl_2.4CuO.5H_2O$; *pseudoboleite*, $5PbCl_2.4CuO.6H_2O$; *phosgenite*, $Pb_2Cl_2CO_3$; *daubreeite*, $BiCl_3.2Bi_2O_3.3H_2O$; and in some Stassfurt minerals, *carnallite*, $KCl.MgCl_2.6H_2O$; *bischofite*, $MgCl_2.6H_2O$; *tachhydrite*, $CaCl_2.2MgCl_2.12H_2O$; *boracite*, $MgCl_2.2Mg_3B_8O_{15}$; etc. Chlorine also occurs in mineral phosphates—*e.g.* it partially replaces fluorine in the *chlorapatites*—*pyromorphite*, $(PbCl)Pb_4(PO_4)_3$; *mimetite*, $(PbCl)Pb_4(AsO_4)_3$; and *vanadinite*, $(PbCl)Pb_4(VO_4)_3$. It occurs in *pyrosmalite*, $H_8(Fe,Mn)_4Si_4O_{16}Cl$; sodalite, $Na_4Al_3Si_3O_{12}Cl$, and other silicate minerals.

Chlorides occur in sea, river, and spring water, and small quantities in rain water. The ashes of plants and animals contain some chlorides. The gastric juices of animals contain chlorides as well as free hydrochloric acid. The 0·2 to 0·4 per cent. of free hydrochloric acid in the gastric juices of man is thought to play an important *rôle* in the digestion of food.[3] Sodium chloride occurs in blood and in urine; flesh contains potassium chloride; while milk contains both of the alkaline chlorides, with potassium chloride in large excess. According to R. Wanach,[4] blood contains 0·259 per cent. of chlorine, and serum, 0·353 per cent.; and according to A. J. Carlson, J. R. Greer, and A. B. Luckhardt, there is still more chlorine in lymph. T. Gassmann found human teeth to contain 0·25 to 0·41 per cent. of combined chlorine, and the teeth of animals rather less.

Bromine.—J. H. L. Vogt[5] estimates that bromine occupies about the 25th place in the list of elements arranged in the relative order of their abundance; and that the total crust of the earth has about 0·001 per cent. of bromine—the solid portion 0·00001 per cent. The ratio of bromine to chlorine is about the same in sea water and in the solid crust, and amounts to 1 : 150. The ratio of chlorides to

bromides in marine waters of the globe is almost constant, excepting land-locked seas like the Black and Baltic Seas. It has been estimated that there are about 120000,000000 tons of bromides present in all the marine waters of our globe. The salt lake south of Gabes in Tunis has been worked since 1915 for bromine and potash.

There is no record of the occurrence of free bromine in nature, but R. V. Matteucci[6] has reported the presence of hydrogen bromide in the fumeroles about Vesuvius. Bromine usually occurs as an alkali bromide or as silver bromide with more or less silver chloride and silver iodide. Thus, the Chilean mineral *bromargyrite*, *bromyrite*, or *bromite* approximates to AgBr; chlorobromosilver or *embolite*, Ag(Cl,Br); and *iodobromite*, or *iodoembolite*, Ag(Cl,Br,I). Small quantities of these minerals occur in other places. Bromine has been reported in rock salt, meerschaum, and in French phosphorites by F. Kuhlmann;[7] in Silesian zinc ores by C. F. Mentzel and M. Cochler; in Chili saltpetre by H. Grüneberg; in coal by A. Duflos; and in ammonia water and artificial sal ammoniac, by C. Mène and others. The Stassfurt salts contain bromides, indeed, these salts are the chief source of commercial bromine.[8] Perhaps two-thirds of the world's annual consumption of bromine (1,500,000 kilos) was obtained in Germany from these deposits. According to H. E. Boeke, the bromine in the Stassfurt deposits is there in the form of a *bromo-carnallite*, $MgBr_2.KBr.6H_2O$, in isomorphous mixture with carnallite $MgCl_2.KCl.6H_2O$. L. W. Winkler reported that the potash liquors of sp. gr. 1·3, from Stassfurt, Mecklenberg, and Hainleite respectively, have 7·492, 5·398, and 3·691 grms. per litre. Bischofite and tachhydrite from Vienenburg are the richest in bromine and contain respectively 0·467 and 0·438 per cent.; carnallite has 0·143 to 0·456 per cent.; sylvine, 0·117 to 0·360 per cent.; sylvinite, 0·085 to 0·331 per cent.; Hartsalz, 0·027 per cent.; and langbeinite, 0·016 per cent. The presence of bromides has been detected in numerous mineral and spring waters. There is a long list of reported occurrences of bromine in mineral waters in different parts of the world arranged alphabetically in L. Gmelin and K. Kraut's *Handbuch der anorganischen Chemie* (Heidelberg, 1. ii, 218, 1909). The waters of Anderton (Cheshire), Cheltenham (Gloucester), Harrogate (Yorkshire), Marston, Wheelock, and Winsford (Cheshire) are in the list for England. Some of the brine springs—*e.g.* the Congress and Excelsior Springs of Saratoga, N.Y.; Natrona (Wyoming); Tarentum (Pennsylvania); Mason City, Parkersville, etc. (West Virginia); Michigan, Pittsburg, Syracuse, Pomeroy, etc. (Ohio)—contain so large an amount of bromine that in importance they are second only to the Stassfurt deposits as sources of commercial supply; and they have played an important part in keeping down the price, and preventing the Stassfurt syndicate monopolizing the world's markets. The mineral waters of Ohio are said to contain the eq. of from 3·4 to 3·9 per cent. of magnesium bromide. Bromine is present in sea water. The mixture of salts left on evaporation of the waters of the Atlantic Ocean contains from 0·13 to 0·19 per cent. of bromine—presumably as magnesium bromide; the Red Sea, 0·13 to 0·18; the Caspian Sea, 0·05; and the Dead Sea, 1·55 to 2·72 per cent. of bromine.[9]

E. Marchand[10] has reported the presence of traces of bromine in rain and snow. The ashes of many sea weeds and sea animals contain bromine—thus, dried *Fucus vesiculosus* contains 0·682 per cent. of bromine.[11] Bromine has been reported in human urine, salt herrings, sponges, and cod liver oil; but not in bone ash. Indeed, all products directly or indirectly derived from sea-salt or from Stassfurt deposits—in the present or in the past—contain bromine. It is also said to be an essential constituent of the dye Tyrian purple which was once largely obtained from a species of marine gastropod or mollusc.

Iodine.—Iodine is perhaps the least abundant of the halogens. Although widely distributed, it always occurs in small quantities. J. H. L. Vogt[12] estimates there is about 0·0001 per cent. of iodine in the earth's crust—the solid matter containing about 0·00001 per cent.; and the sea, 0·001 per cent. A. Gautier's estimate of the iodine in the sea is about one-fifth of this. Iodine occupies the

28th place in the list of elements arranged in their relative order of abundance; so that iodine has exercised no essential chemical or geological influence on the earth's surface. The sea appears to be the great reservoir of iodine. The ratio of bromine to iodine in sea water and in the solid crust is approximately the same, *viz.* from 1 : 10 to 1 : 12; and, in sea water, the ratio of chlorine to iodine is as 1 : 0·00012. L. W. Winkler reported 17 mgrms. of iodine (as iodide) per litre of a natural saline water from Mecklenburg, that is, about 340 times as much as in sea water; a sylvinite mother-liquor from Alsace contained 0·5 mgrm. of iodine per litre.

Iodine does not occur free in nature, although, according to J. A. Wanklyn,[13] the waters of Woodhall Spa (Lincoln) are coloured brown by this element. R. V. Matteucci reported the occurrence of hydrogen iodide in the emanations of Vesuvius, and A. Gautier found iodine in the gases disengaged from cooling lava. Iodine occurs along with bromine in *iodobromite*, Ag(Cl, Br, I); in *iodyrite*, AgI; *marshite*, CuI; *coccinite*, HgI_2; and in *schwartzembergite*, $Pb(I, Cl)_2.2PbO$. According to A. Guyard,[14] the iodine—up to about 0·175 per cent. in Chile saltpetre—is present as sodium iodate, $NaIO_3$, and periodate, $NaIO_4$; H. Grüneberg considers a double iodide of sodium and magnesium is also present. Potash saltpetre also has been reported to contain potassium iodate, KIO_3, the *caliche* from which Chile saltpetre is extracted forms one of the most important sources of iodine; it contains about 0·2 per cent. of iodine, probably as sodium iodate. Iodine has also been reported in the lead ores of Catorce (Mexico);[15] in malachite—0·08 to 0·40 per cent. (W. Autenrieth); Silesian zinc ores (C. F. Mentzel and M. Cochler); the clay shales of Latorp in Sweden (J. G. Gentele); the limestones of Lyon and Montpellier (G. Lembert); the bituminous shales of Wurtemberg (G. C. L. Sigwart); the dolomites of Saxony (L. R. Rivier von Fellenberg); rock salt (O. Henry); the phosphorites of France (F. Kuhlmann); the phosphates of Quercy (H. Lasne); granites (A. Gautier); Norwegian apatite (A. Gautier); coal, and ammonium salts derived from coal (A. Duflos); guano of Curaçao (H. Steffens); and the Stassfurt salt deposits (A. Frank)—although F. Rinne and E. Erdmann failed to confirm A. Frank's results. The presence of iodides has also been recorded in a number of spring waters, brines, etc.[16] In Great Britain it occurs in the waters of Leamington (Warwickshire), Bath (Somerset), Cheltenham (Gloucester), Harrogate (Yorkshire), Woodhall Spa (Lincoln), Bonnington (near Leith), Shotley Bridge (Durham), etc. Iodine occurs in small quantities in sea water; E. Sonstadt[17] estimated that there is about one part of calcium iodate per 250,000 parts of sea water; but according to A. Gautier, the iodine in the surface water of the Mediterranean Sea is found only in the organic matter which can be separated from the water itself by filtration; but at depths below 800 metres, he found iodine to be in water itself as soluble iodides. According to A. Gautier, also, the waters of the Atlantic contain 2·240 mgrms. per litre; and according to L. W. Winkler, the waters of the Adriatic Sea, 0·038 mgrm. per litre. A. Goebel reported 0·11 per cent. of iodine in the salts from Red Lake (Perekop, Crimea); and H. Fresenius 0·0000247 per cent. in the waters of the Dead Sea. The amount is so small that analysts have usually ignored the iodine, or reported mere traces. Similar remarks apply to the brines from the waters of closed basins.

Iodine has been reported in rain and snow,[18] and A. Chatin found iodine universally present in small quantities in the atm., rain water, and running streams. A. Gautier reported in 1889 that the air of Paris contained less than 0·002 mgrm. of free iodine or an iodine compound in about 4000 litres; but 100 litres of air in Paris contained 0·0013 mgrm. in a form insoluble in water, generally the spores of algæ, mosses, lichens, etc., suspended in the air. A. Gautier also found sea air to contain 0·0167 mgrm. of iodine per 100 litres. The amount of iodine in mountain air and the air of forests is less than in other parts. The iodine in the atm. is supposed to be of marine origin. The presence of iodine as a normal constituent of the atm. has been denied,[19] but A. Chatin's conclusions were confirmed by J. A. Barral, A. A. B. Bussy, and A. Gautier. Marine animals and plants assimilate

iodine from sea water; most of the iodine can be extracted by water from the ash of these organisms. It appears strange that the marine algæ should select iodine from sea water and practically leave the bromine which is present in much larger proportions. The pelagic seaweeds (algæ) in favourable localities cover the ocean about the 10-fathoms line with dense fields of floating foliage; the littoral seaweeds grow nearer shore at about the limit of extreme low tide. The deep-sea algæ usually have a greater proportion of iodine than those which grow in shallow water. According to E. C. C. Stanford,[20] the percentage amounts of iodine in a few dried plants are as follows:

Littoral (Shore) Seaweeds		Pelagic (Deep-sea) Seaweeds	
Fucus filium	0·089	Nereocystis leutkeana	0·521
Fucus digitatus	0·135	*Macrocystis pyrifera*	0·205
Fucus nodosus	0·057	Pelagophycus porra	0·241
Fucus serratus	0·085	Laminaria digitata	0·374
Fucus vesiculosus	0·001	Laminaria stenophylla	0·478
Ulva umbilicalis	0·059	Laminaria saccharina	0·255

A. M. Ossendowsky studied the algæ employed in northern Japan for making iodine. According to J. Pellieux, seaweed grown in winter usually carries more iodine than that grown in summer; that grown in the north more than that grown in the south; and the younger parts of the algæ more than in the older parts. Iodine has not been found in the gelatinous varieties of marine algæ—*e.g.* the *chondrus crispus* or Irish moss, and the *eucheuma spinosum* or agar-agar; nor has it been found in the *enteromorpha compressa*, or common sea-grass. Some plants which grow near the sea—*e.g.* the *salsola kali*, or salt-wort of salt-marshes, from which *barilla* is made[21]—are almost free from iodine. Smaller amounts of iodine have been found in fresh-water plants than in land plants, and smaller proportions of potash are found in them also. According to A. Gautier,[22] iodine must be a constituent of the chlorophyll or reserve protoplasm of plants because plants containing chlorophyll contain more than the algæ and fungi which are free from chlorophyll. Iodine is found in tobacco (A. Gautier), and in beetroot (M. J. Personne), and the potash derived from these products, as well as other plants, also contains iodine. It is found in fossil plants: and hence also its occurrence in coal, and in the ammoniacal products derived from coal.

Turkey sponge has 0·2 per cent., the honeycomb sponge 0·054 per cent., and according to F. Hundeshagen,[23] the sponges from tropical seas contain up to 14 per cent. of iodine; A. Fyfe, and K. Stratingh found none in corals; but E. Drechsel isolated from certain corals what he considered to be *iodogorgic acid*, $C_4H_8INO_2$. Minute quantities of iodine have also been reported in nearly all marine worms, molluscs, fish, and other marine animals which have been examined. For example, oysters have been reported with 0·00004 per cent. of iodine; prawns, 0·00044; cockles, 0·00214; mussels, 0·0357; salt herrings, 0·00065; cod-fish, 0·00016; and cod's liver, 0·00016 per cent. It occurs in most fish oils—cod-liver oil, for instance, contains from 0·0003 to 0·0008 per cent. of iodine; whale oil has 0·0001 per cent.; and seal oil, 0·00005 per cent.

Iodine is a normal constituent of animals where it probably occurs as a complex organic compound. The iodine of the thyroid gland is present as a kind of albumen containing phosphorus and about 9 per cent. of iodine. This has been isolated by digesting the gland with sulphuric acid, and precipitating with alcohol. The iodine seems to play a most important part in the animal economy. The proportion of iodine is smaller in young people than in adults, and the amount becomes less and less with the aged.[24] According to J. Justus, the amount of iodine in milligrams per 100 grms. of the various organs of human beings is: thyroid gland, 9·76 mgrms.; liver, 1·214; kidney, 1·053; stomach, 0·989; skin, 0·879; hair, 0·844; nails, 0·800; prostate, 0·689; lymphatic gland, 0·600; spleen, 0·560; testicle, 0·500; pancreas, 0·431; virginal uterus, 0·413; lungs, 0·320; nerves, 0·200; small

intestine, 0·119; fatty tissue, traces. The proportion in the corresponding parts of animals is smaller. Only a very small proportion is found in blood and muscle. O. Loeb[25] could find none in the brains, spinal marrow, fat, and bones. Iodine has been reported in wine and in eggs. E. Winterstein found no iodine in milk, cheese, or cow's urine; but he found iodine in thirty-five phanerogams in beetroot, celery, lettuce, and carrots, but not in mushrooms or yellow boletus.

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§ 6. The History of Chlorine, Bromine, and Iodine

La vrai chimie ne date que de l'emploi bien établi des acides minéraux, qui sont veritables dissolvants des metaux.—F. HOEFER (1842).

Sodium chloride was known as salt from the earliest times. About 77 A.D., Pliny, in his *Naturalis Historiæ* (**33**. 25), described the purification of gold by heating it with salt, misy (iron or copper sulphate), and schistos (clay). This mixture would give off fumes of hydrogen chloride. The attention, however, was focussed on the effect of the treatment on the metal; no notice was taken of the effluvia. In the *Alchimia Geberi* (Bern, 1545)—supposed to have been written in the thirteenth century or afterwards—there is an account of the preparation of nitric acid by distilling a mixture of saltpetre, copper sulphate, and clay; and Geber adds that the product is a more active solvent if some *sal ammoniacus* is mixed with the ingredients. Thus Geber prepared *aqua regia*. Raymond Lully [1] called the former *aqua salis nitri*, and the latter *aqua salis armoniaci*; Albertus Magnus [2] called the first *aqua prima* (nitric acid), the second *aqua secunda* (aqua regia). J. R. Glauber (1648) [3] prepared aqua regia by distilling nitric acid with common salt.

While the Arabian alchemists were probably acquainted with the mixture of nitric and hydrochloric acid known as aqua regia, there is nothing to show that they were acquainted with hydrochloric acid. The method of making hydrochloric acid, first called *spiritus salis*, dates from the end of the sixteenth century. Although there is no record, this acid was probably made earlier than this because it was the custom of the then chemists to collect the products of the distillation of mixtures of various salts and earths; and the necessary ingredients were in their hands. For example, in preparing aqua regia it merely required the substitution of *sal naturus* for *nitrum*—which, as Pliny said, "do not greatly differ in their properties"—to furnish *spiritus salis*. It is almost inconceivable that this was not done. The preparation of the acid by distilling salt with clay is mentioned in the *Alchemia* (Francofurti, 1595) of A. Libavius; and in the *Triumphwagen des Antimonii* (Leipzig, 1624) of the anonymous writer Basil Valentine. J. R. Glauber (1648) described the preparation of *spiritus salis* by distilling common salt with oil of vitriol or with alum. J. R. Glauber also described the salient properties of this acid, and especially remarked on its solvent action on the metals. He mentioned that silver resists its action. H. Boerhaave knew that lead resists the action of the acid; R. Boyle referred to the action of the acid on soln. containing silver, and he noted that the salt which this acid forms with the alkalies effervesces and fumes when treated with sulphuric acid. Stephen Hales (1727) noticed that a gas very soluble in water is given off when sal ammoniac is heated with sulphuric acid, and, in 1772, J. Priestley collected the gas over mercury and called it *marine acid air* in reference to its production from sea-salt. For a similar reason, the French term for the acid was *acide marin*. In A. L. Lavoisier's nomenclature (1787), the acid was designated *acide muriatique*, or *muriatic acid*; and after H. Davy's investigations on chlorine, the name was changed to *acide chlorhydrique* or *hydrochloric acid*.

There can be little doubt that the corrosive, suffocating, greenish-yellow fumes of chlorine must have been known onwards from the thirteenth century by all those who made and used aqua regia—*e.g.* J. R. Glauber's rectified spirit of salt mentioned above. Early in the seventeenth century, J. B. van Helmont mentioned that when *sal marin* (sodium chloride) or *sal armeniacus* (ammonium chloride) and

aqua chrysulca (nitric acid) are mixed together, a *flatus incoercibile* is evolved. J. Glauber (1648) also appears to have obtained a similar gas by heating zinc chloride and sand; he also said that by distilling spirit of salt with metal oxides, he obtained in the receiver a spirit the colour of fire, which dissolved all the metals and nearly all minerals. This liquid was no doubt chlorine water; J. R. Glauber called it *rectified spirit of salt*, and he said that it can be used for making many products useful in medicine, in alchemy, and in the arts. He gives an example by pointing out that when treated with alcohol, spirit of salt furnishes *oleum vini*, which is very agreeable, and an excellent cordial.

The meaning of these observations was not understood until C. W. Scheele published his *De magnesia nigra*[4] in 1774. C. W. Scheele found that when hydrochloric acid is heated with manganese dioxide, a yellowish-green gas, with a smell resembling warm aqua regia, is given off. C. W. Scheele's directions for preparing the gas are:

Common muriatic acid is to be mixed with levigated manganese (*i.e.* pyrolusite) in any quantity in a glass retort, which is to be put into warm sand, and a glass receiver applied, capable of containing about 12 oz. of water. Into the receiver put about 2 drms. of water; the joints are to be luted with a piece of blotting paper tied round them. In a quarter of an hour, or a little longer, a quantity of the acid, going over into the receiver, gives the air contained in it a yellow colour, and then it is to be separated from the retort.

He remarked that the gas is soluble in water; that it corroded corks yellow as if they had been treated with nitric acid; that it bleached paper coloured with litmus; that it bleached green vegetables, and red, blue, and yellow flowers nearly white, and the colour was not restored by treatment with acids or alkalies; that it converted mercuric sulphide into the chloride and sodium hydroxide, common salt; etc.

C. W. Scheele considered the yellowish-green gas to be muriatic acid freed from hydrogen (then believed to be phlogiston); accordingly, in the language of his time, it was called *dephlogisticated muriatic acid*. A. L. Lavoisier (1789)[5] named the gas **oxymuriatic acid**, or oxygenated muriatic acid, because he considered it to be an oxide of muriatic (*i.e.* hydrochloric) acid; and, consistent with his oxygen theory of acids, A. L. Lavoisier considered muriatic acid to be a compound of oxygen with an hypothetical **muriatic base**—**murium**; this imaginary element was later symbolized Mu; hydrochloric acid was symbolized MuO_2; and C. W. Scheele's gas, MuO_3. Hence, added A. L. Lavoisier, muriatic and oxymuriatic acids are related to each other like sulphurous and sulphuric acids; and he was at first inclined to call the one *acide muriateux*, and the other *acide muriatique*. This certainly seemed to be the most plausible explanation of the reactions. Lavoisier's hypothesis was supported by an observation of C. L. Berthollet (1785),[6] that if the manganese dioxide be deprived of some of its oxygen by calcination, it furnishes a much smaller quantity of Scheele's gas. Hence, concluded C. L. Berthollet, "it is to the vital air (oxygen) of the manganese dioxide, which combines with the muriatic acid, that the formation of dephlogisticated marine acid is due." He did not succeed in oxidizing muriatic acid to oxymuriatic acid, because he considered that the elastic state of muriatic acid gas prevents it uniting directly with oxygen. However, C. L. Berthollet supposed that he had succeeded in decomposing dephlogisticated marine acid into muriatic acid and oxygen, for he noticed that an aq. soln. of C. W. Scheele's gas—the so-called oxymuriatic acid—when exposed to sunlight, gives off bubbles of oxygen gas, and forms muriatic acid.

In 1800, W. Henry[7] passed electric sparks through muriatic acid gas and obtained a little hydrogen which he supposed to come from the moisture in the gas; on sparking a mixture of oxygen and muriatic acid gas he obtained a little oxymuriatic acid gas which he supposed was formed by the electric sparks decomposing some of the moisture in the muriatic acid gas into oxygen, and the union of the oxygen with the muriatic acid gas to form oxymuriatic acid gas. The experiments

of J. L. Gay Lussac and L. J. Thénard,[8] *and the* earlier experiments (1809) of *H. Davy,*[9] were complicated by the assumption that muriatic acid gas contains water, or the principles which constitute water, intimately combined. According to J. L. Gay Lussac and L. J. Thénard, muriatic acid gas and oxygen are formed when a mixture of steam and oxymuriatic acid is passed through a heated porcelain tube. It was here assumed that the muriatic acid gas in virtue of its great affinity for water, leaves the oxygen with which it is combined in oxymuriatic acid gas, and combines with the water to form muriatic acid gas. L. J. Gay Lussac and L. J. Thénard also found that by heating a mixture of hydrogen and oxymuriatic acid gas, there is a " violent inflammation with the production of muriatic acid " ; they also showed that a mixture of equal volumes of hydrogen and oxymuriatic acid gas does not change in darkness, but in light, the mixture is transformed into muriatic acid ; and in bright sunlight, the combination is attended by a violent explosion. It was assumed in these experiments that water is formed by the hydrogen removing the necessary oxygen from oxymuriatic acid gas, and leaves behind muriatic acid gas which is eager to combine with water. J. L. Gay Lussac and L. J. Thénard also tried to deoxidize oxymuriatic acid, so as to isolate the hypothetical muriatic base of A. L. Lavoisier, by passing the dry gas over red-hot carbon, but when the carbon was freed from hydrogen no change was observed even though " urged to the most violent heat of the forge." In any case, the attempt to separate from oxymuriatic acid anything but itself was a failure. While favouring Lavoisier's hypothesis, J. L. Gay Lussac and L. J. Thénard added : " the facts can also be explained on the hypothesis that oxymuriatic acid is an elementary body." Here, then, are two rival hypotheses as to the nature of oxymuriatic acid - the yellowish-green gas discovered by Scheele ! According to C. W. Scheele's hypothesis, oxymuriatic acid = muriatic acid less hydrogen ; according to C. L. Berthollet and A. L. Lavoisier's hypothesis, oxymuriatic acid = muriatic acid plus oxygen.

In his *Researches on the Oxymuriatic Acid* (1810), H. Davy described the attempts which he made, without success, to decompose oxymuriatic acid gas. He also found that when dried muriatic acid gas is heated with metallic sodium or potassium, the metallic muriate and hydrogen are formed, but neither water nor oxygen is obtained. Hence, no oxygen can be found in either muriatic acid gas or oxymuriatic acid gas. H. Züblin also tried in 1881, and likewise failed to decompose chlorine. Accordingly, H. Davy claimed that C. W. Scheele's view is an expression of the facts, while Lavoisier's theory, though " beautiful and satisfactory," is based upon a dubious hypothesis - *viz.* the presence of oxygen in gases where none can be found. The definition of an element will not permit us to assume that oxymuriatic acid is a compound, because, in spite of repeated efforts, nothing simpler than itself has ever been obtained from the gas. In order to avoid the hypothesis implied in the term oxymuriatic acid, H. Davy proposed the alternative term chlorine and symbol Cl—from the Greek χλωρὸς, green. The term chlorine is thus " founded upon one of the obvious and characteristic properties of the gas—its colour."

According to H. Davy's theory, C. L. Berthollet's observation on the action of oxymuriatic acid gas on water, and J. L. Gay Lussac and L. J. Thénard's observation of the action of steam on oxymuriatic acid-gas, are explained by the equation : $2H_2O+2Cl_2=4HCl+O_2$; that is, the oxygen comes from the water, not from the chlorine. Similarly, the formation of chlorine by the action of oxidizing agents upon hydrochloric acid is due to the removal of hydrogen. In symbols : $4HCl+O_2=2H_2O+2Cl_2$. H. Davy also showed that muriatic acid gas when adequately dried contains nothing but hydrogen and chlorine, and he showed that when the gas is decomposed by heating it with mercury, potassium, zinc, or tin, a chloride of the metal is formed, and one volume of hydrogen chloride furnishes half a volume of hydrogen—the other half volume must be chlorine. H. Davy summarized his conclusions from these and other experiments : " There may be oxygen in oxymuriatic gas, but I can find none " ; the hypothesis that oxymuriatic acid is a simple substance, and that muriatic acid is a compound of this substance with hydrogen,

explains all the facts in a simple and direct manner; the alternative hypothesis of the French school rests, in the present state of our knowledge, on hypothetical grounds. The French hypothesis died a lingering death. J. J. Berzelius in 1813[10] tried to argue that the French schools were right; he even expressed his surprise that Davy's hypothesis "could ever gain credit." J. J. Berzelius seems to have misunderstood H. Davy's experiments, but he too accepted Davy's conclusions a few years later. H. Davy's theory is orthodox to-day. New facts as they arrived have fallen harmoniously into their places and arranged themselves about Davy's theory as naturally as do the particles of a salt in solution about the enlarging nucleus of a crystal.

Iodine.—During the Napoleonic wars, nitre beds were cultivated in various parts of France, and from these saltpetre was obtained artificially. About 1811, Bernard Courtois, a manufacturer of saltpetre, near Paris, used an aq. extract of varec or kelp for decomposing the calcium nitrate from the nitre beds; he noticed that the copper vats in which the nitrate was decomposed were rapidly corroded by the liquid, and he traced the effects to a reaction between the copper and an unknown substance in the lye obtained by extracting the varec or kelp with water. B. Courtois isolated this new substance and ascertained its more obvious properties. In his paper entitled *Découverte d'une substance nouvelle dans le vareck*, and published about two years after his discovery,[11] he said:

> The mother-liquors of the lye obtained from varec contain a tolerably large quantity of a singular and curious substance. It can easily be obtained. For this purpose it is sufficient to pour sulphuric acid upon the mother-liquid and to heat the whole in a retort connected with a receiver. The new substance which, on the addition of the sulphuric acid, is at once thrown down as a black powder is converted on heating into a vapour of a superb violet colour; this vapour condenses in the tube of the retort and in the receiver in the form of brilliant crystalline plates, having a lustre equal to that of crystallized lead sulphide. On washing these plates with a little distilled water the substance is obtained in a state of purity. The wonderful colour of its vapour suffices to distinguish it from all other substances known up to the present time, and it has further remarkable properties which render its discovery of the greatest interest.

B. Courtois communicated tidings of this discovery to F. Clément and J. B. Désormes, and they published some results of their study of this new substance early in December, 1813;[12] a few days later J. L. Gay Lussac, who also had received some of B. Courtois' preparation, gave a preliminary account of some researches on B. Courtois' new substance, at a meeting of *l'Institut Imperial de France* on Dec. 6th, 1813. In this communication, J. L. Gay Lussac demonstrated some striking analogies between Courtois' preparation and chlorine; he made clear its elementary nature; and designated it *iode*, the French eq. of its present name—from the Greek ἰωειδής, violet. Its hydrogen compound was prepared and likewise given the very name which it has to-day. J. L. Gay Lussac said:

> After this account one can only compare *iode* with *chlore*, and the new gaseous acid with muriatic acid. . . . The phenomena of which we have just spoken can all be explained either by supposing that *iode* is an element and that it forms an acid when it combines with hydrogen, or by supposing that the latter acid is a compound of water with an unknown substance, and that iode is this substance combined with oxygen. Considering all the facts recounted, the first view appears more probable than the other, and serves at the same time to give probability to that hypothesis according to which oxygenated muriatic acid is regarded as a simple body. Adopting this hypothesis hydriodic acid appears a suitable name for the new acid.

On Dec. 20th, 1813, J. L. Gay Lussac[13] read a further memoir on the combinations of the new element with oxygen; on March 21st, 1814, J. J. Colin and H. G. de Claubry communicated observations made in J. L. Gay Lussac's laboratory on the action of iodine on organic compounds; by June 4th, 1814, L. N. Vauquelin had studied the action of iodine on ammonia, iron, mercury, and alcohol; and finally, on Aug. 1st, 1814, J. L. Gay Lussac communicated his famous *Mémoire sur l'iode*.[14] In this

paper, said F. D. Chattaway,[15] the whole chemical behaviour of iodine is described in such a masterly fashion that it remains to this day a model of what such an investigation ought to be.

H. Davy played a not too glorious part in the history of iodine, and his action roused the ire of J. L. Gay Lussac. Humphry Davy was in Paris at the very time of the excitement consequent on these reports of the properties of B. Courtois' new element; H. Davy received a complimentary specimen from A. M. Ampère on Nov. 23rd, 1813, and on Dec. 11th, 1813, details of his observations on this substance were also communicated by M. le Chevalier Cuvier to *l'Institut Imperial de France*. H. Davy confirmed the conclusions of J. L. Gay Lussac read at l'Institut seven days previously. H. Davy sent a fuller account to the Royal Society,[16] Jan. 20th, 1814, and another on June 16th, 1814, and yet a third on April 20th, 1815. In these memoirs, says F. D. Chattaway, "H. Davy did little more than make the discoveries of B. Courtois and J. L. Gay Lussac known in England." In 1881, H. Züblin tried to decompose iodine, but failed.

It must be added that in 1767, in a paper on *La soude de varech*, L. C. Cadet[17] spoke of a blue and green substance which is obtained by treating the aq. extract of varec by sulphuric or nitric acid; and he attributed the cause of the coloration *à une surabondance d'une terre jaune martial*. F. Hoefer asks: *aurait-il entrevu l'existence de l'iode?*

Bromine.—Of the three halogens, chlorine, bromine, and iodine, bromine has the least eventful history. Its elemental nature and its relation to chlorine and iodine were recognized from the very first. While studying the mother-liquid which remains after the crystallization of salt from the water of the salt-marshes of Montpellier, A. J. Balard was attracted by the intense yellow coloration developed when chlorine water is added to the liquid. A. J. Balard digested the yellow liquid with ether; decanted off the supernatant ethereal soln.; and treated this with potassium hydroxide. The colour was destroyed. The residue resembled potassium chloride; but unlike the chloride, when heated with manganese dioxide and sulphuric acid it furnished red fumes which condensed to a dark brown liquid with an unpleasant smell.

A. J. Balard submitted a *pli cacheté* to the *Académie des Sciences* in 1824, and published an account of his work in his *Mémoire sur une substance particulière contenue dans l'eau de la mer*,[18] in 1826. He related that he was at first inclined to regard the substance as a chloride of iodine, but he tried in vain to establish the presence of iodine. He said:

Its refusal to colour starch blue, and the white precipitate which it formed with the protonitrate of mercury and with nitrate of lead assured me that no iodine was contained in it. On the other hand, I could not detect any indication of decomposition when it was submitted successively to the action of the voltaic pile and to high temp. Such a resistance to decomposition could not fail to suggest to me the idea that I had to deal with a simple body, or with one comporting itself as a simple body, and indeed I was confirmed in this view when I regarded the entire treatment to which I had subjected the substance. I came, therefore, to the conclusion that I had found out a new simple substance closely resembling chlorine and iodine in its chemical aptitudes, and forming absolutely analogous compounds, but showing marked points of difference from them both in its physical properties and chemical behaviour, and clearly to be distinguished from them.

At first, A. J. Balard called this substance *muride*, but afterwards *bromine*—from the Greek *βρῶμος*, a stench. A. J. Balard prepared hydrobromic, hypobromous, and bromous acids; and he concluded his memoir by summing up the arguments in favour of the elementary nature of bromine:

A substance which in the free state resists as effectively as does bromine all attempts to decompose it, which is expelled by chlorine from all its compounds possessed of exactly its original properties, which when allowed to act on compounds containing iodine substitutes itself in every case for the latter element to play a similar part in the new products, and which [illegible]s of action, is connected with both chlorine and iodine

by the most sustained analogies, seems to possess the same right to be considered as a simple body. If these results are confirmed by other chemists, bromine must as a simple body rank along with chlorine and iodine, and it is manifestly between these elements that it must be placed.

J. R. Joss[19] seems to have obtained this element in 1824; he noticed that a red colour was developed in preparing hydrogen chloride by heating a sample of rock salt with sulphuric acid, but he attributed the coloration to the presence of selenium in the acid employed. J. Volhard also narrates that J. von Liebig had bromine in hand a month before A. J. Balard, but mistook it for iodine chloride:

J. von Liebig related that some years before Balard's discovery he received, from a salt manufactory in Germany—the Kreuznacher salt springs—a vessel containing bromine, or at least a product very rich in bromine, with a request to examine it. Believing the liquid to be iodine chloride, he did not subject the specimen to a very exhaustive study. When he heard of the discovery of Balard, Liebig saw his blunder, and placed the vessel in a special cabinet for storing mistakes—*l'armoire des fautes*. Liebig pointed this out to his friends to show how easily one could get very close to a discovery of the first rank and yet fail to grasp the facts when guided by preconceived ideas.

In 1881, H. Züblin tried to decompose bromine into simpler constituents, but failed.

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§ 7. The Preparation of Chlorine

Chlorine is nearly always prepared in the laboratory by the action of an oxidizing agent—manganese dioxide, lead dioxide, barium dioxide, potassium dichromate,

potassium permanganate, air, etc.—either directly on hydrochloric acid, or indirectly through the medium of a chloride. Manganese dioxide is the oxidizing agent most commonly used. *Much chlorine is prepared for industrial purposes by the electrolysis of soln. of sodium chloride.*

I. The preparation of chlorine by the action of heat on the chlorides of the heavy metals.—Gold and platinum chlorides give off chlorine when heated, but these compounds are far too expensive for the preparation of chlorine, except for very *special purposes, such as V. and C. Meyer's work*[1] *on the vapour density of chlorine,* where platinous chloride, $PtCl_2$, was used as the source of chlorine: $PtCl_2 \rightarrow Pt + Cl_2$. This salt was selected because it is easily decomposed—about 360°—and is not deliquescent. If moisture be present, some hydrogen chloride and oxygen will be formed. W. Wahl (1913) used gold chloride. M. Wildermann passed purified *chlorine through a tube of hard glass containing reduced copper: cupric chloride,* $CuCl_2$, is formed. The chlorine was washed out of the tube by dry air; the tube was sealed at one end; and heated by a combustion furnace. Chlorine gas was evolved: $2CuCl_2 \rightarrow 2CuCl + Cl_2$. In special cases, too, highly purified fused silver chloride can be electrolyzed to furnish chlorine of a high degree of purity.[2]

II. The preparation of chlorine by the oxidization of hydrochloric acid.—1. *Manganese dioxide.*—C. W. Scheele, the discoverer of chlorine, obtained this gas by warming manganese dioxide with hydrochloric acid: a mixture of sulphuric acid with manganese dioxide and sodium chloride may also be used. In the latter case, *a mixture of one part of pyrolusite with from* 1·5 to 2·5 parts of sodium chloride and 2·5 to 3 parts of conc. sulphuric acid dil. with its own volume of water is made.[3] The equation representing the reaction is: $MnO_2 + 2NaCl + 2H_2SO_4 = MnSO_4 + 2H_2O + Na_2SO_4 + Cl_2$, but some manganese chloride, $MnCl_2$, and sodium bisulphate may be simultaneously formed. In Scheele's process, the mixture may contain one part pyrolusite with four parts of commercial acid, or an excess of coarsely crushed fragments of the pyrolusite may be used; and after the process is over, the excess can be washed and used again. The end products of the reaction are indicated in the equation: $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. The manganese dioxide, or the mixture of manganese dioxide, and salt is placed in a flask *A*, Fig. 4, fitted with a wash-bottle, *C*, or other washing and scrubbing train, and the acid poured into the tube funnel, *B*. The gas cannot be collected over mercury because that metal is immediately attacked by chlorine forming the chloride. For lecture experiments, the gas can be collected over warm water, or water sat. with salt, or by the upward displacement of the air. The preparation under these conditions should be conducted in a well-ventilated fume chamber since the gas is most objectionable in the atm.

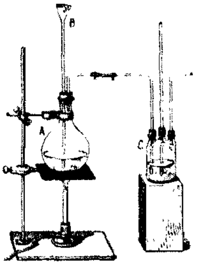

FIG. 4.—The Preparation of Chlorine.

The purification of chlorine.—The gas can be washed with water in order to remove most of the fumes of hydrogen chloride carried over with the chlorine, but to remove the last traces of hydrogen chloride, F. Stolba[4] recommended the introduction of a wash bottle with a soln. of copper sulphate, or a tube of solid copper sulphate or bleaching powder, and then washing the gas with water. According to A. Michaelis, the bleaching powder contaminates the gas with hypochlorous acid. F. Mohr recommended removing the gas by scrubbing it in a tube packed with manganese dioxide, and H. Moissan and A. B. du Jassonneix kept the tube warm at about 50°. With the same object, W. Hampe and H. Ditz washed the gas in a conc. soln. of potassium permanganate. To avoid contamination with carbon dioxide, H. Ditz recommended washing the manganese dioxide first with nitric or dilute sulphuric acid and then with water to remove carbonates. F. P. Treadwell

and W. A. K. Christie removed chlorine oxides from the gas by passing it through a tube packed with asbestos, heated to redness. The gas can be dried by conc. sulphuric acid, calcium chloride, or phosphorus pentoxide. J. A. Harker[6] still further purified chlorine by passing the purified gas into cold water so as to form the hydrate, $Cl_2.8H_2O$, which was found to keep very well in darkness below 9°. When the hydrate is warmed slightly, it gives off chlorine with less than 0·2 per cent. of impurity. H. Moissan and A. B. du Jassonneix purified the dried gas by liquefaction, and, after prolonged contact with calcium chloride, solidifying the liquid so as to enable traces of dissolved gaseous impurities to be pumped off. L. Moser recommended removing air and carbon oxide by liquefying the gas with a freezing mixture of carbon dioxide and ether, and redistilling.

The mechanism of the reaction between manganese dioxide and hydrochloric acid.—The reaction between hydrochloric acid and manganese dioxide has given rise to much discussion. When manganese dioxide is treated with cold conc. hydrochloric acid, a dark brown liquid is formed, and chlorine is slowly evolved at ordinary temp., more quickly if the mixture be warmed. The liquid finally becomes colourless and it contains manganous chloride, $MnCl_2$. G. Förchhammer, in 1821, showed that if the freshly prepared brown liquid be largely diluted with water, it remains clear for a few seconds, and then becomes turbid owing to the formation of a brown precipitate of hydrated manganese dioxide. Quite a similar precipitate is formed if either the red oxide of manganese, Mn_3O_4, or the sesquioxide of manganese, Mn_2O_3, be treated in place of the dioxide, MnO_2. According to S. U. Pickering,[6] however, the composition of the precipitate varies with the conditions of the experiment from about $3MnO_2.MnO$ to $7MnO_2+MnO$. Attempts have been made to find what the brown soln. contains. Most are agreed that either manganese trichloride, $MnCl_3$, or manganese tetrachloride, $MnCl_4$, is first formed as an intermediate product. M. Berthelot[7] considers it improbable that the simple manganese tetrachloride is produced when a soln. of manganous chloride, $MnCl_2$, in hydrochloric acid is treated with chlorine; rather is the first product an easily decomposed perchlorinated compound, $HCl_3.nMnCl_3$ or $MnCl_4.nHCl$. The formation and decomposition of such a product would explain the observed phenomena. The isolation of the product of the reaction has proved very difficult because it decomposes so readily. Indirect evidence has been obtained by determining the ratio of the manganese to the available chlorine; but the results are not decisive; and hence some have considered the trichloride is formed; others, the tetrachloride. C. Naumann isolated the double salts $(NH_4)_2MnCl_5$ and K_2MnCl_5, and hence argued in favour of the trichloride. J. Nicklès[8] treated manganese dioxide suspended in ether, $C_4H_{10}O$, with hydrogen chloride, and obtained a green liquid which changed to a deep violet colour on adding more ether. The green oil has a composition corresponding with $MnCl_4.12C_4H_{10}O.2H_2O$; hence, argued J. Nicklès, the green oil contains manganese tetrachloride. J. Nicklès did not succeed in isolating a definite product, and, since he found his analyses *variaient singulièrement par leur composition*, S. U. Pickering considers that it is just as likely that $MnCl_3.12C_4H_{10}O.2HCl.4H_2O$ might have been present. W. B. Holmes[9] used carbon tetrachloride in place of ether, and obtained both the tri- and tetrachlorides of manganese. He therefore inferred that the reaction between hydrochloric acid and manganese dioxide furnishes a soln. containing both chlorides: $MnO_2+4HCl=MnCl_4+2H_2O$ and $2MnO_2+8HCl=2MnCl_3+Cl_2+4H_2O$; but in conjunction with E. F. Manuel, he gave up the tetrachloride hypothesis, and expressed the belief that the trichloride alone is formed. As an alternative hypothesis, B. Franke assumed that hydrochloromanganic acid, H_2MnCl_6, is formed as an intermediate product: $MnO_2+6HCl=H_2MnCl_6+2H_2O$; which decomposed: $H_2MnCl_6=2HCl+Cl_2+MnCl_2$. In the presence of manganous chloride and an excess of water still more complex reactions occurred, finally furnishing $MnO_2.H_2O$.

Apart from electrolytic chlorine, by far the largest proportion of chlorine used in the industries is made by the oxidation of hydrochloric acid, generally

by manganese dioxide either as native manganese ore, or as "recovered manganese"—the so-called *Weldon mud*.

The process with hydrochloric acid is conducted as an annexe to the salt-cake works where the acid is a by-product of the process—otherwise the cost of transport of hydrochloric acid would not enable the process to live against competitive prices. The stills for *generating* the chlorine are not made of lead because that metal is attacked too readily by the acid; vessels of stoneware were formerly used; to-day the stills are built with flags of siliceous sandstone which are sometimes first boiled in tar. The volvic lava from Puy-de-Dôme (France) is preferred even to the best sandstone. Acid-resisting bricks are also used. The flags are clamped together by iron tie-rods, and the joints either made tight with indiarubber cord, or tongue-and-groove joints are employed with a cement of fireclay and tar. The mixture is heated by blowing in steam. A section of one type of chlorine still is illustrated in Fig. 5. The manganese ore rests on the perforated plate *A*; *B* is a stoneware steam pipe; the steam enters the still *viâ B* below the perforated false bottom; *C* is the exit pipe for chlorine; *D* is a man-hole; *E* an acid safety funnel which has various designs; and *F* is an opening for running off the spent acid, it is closed by a wooden plug. The lid is of lead. The exhausted still liquor contains manganous chloride, and some ferric and other metal chlorides derived from impurities in the manganese ore. There is also some free chlorine, and free hydrochloric acid—*e.g.* the composition of a still liquor approximated:

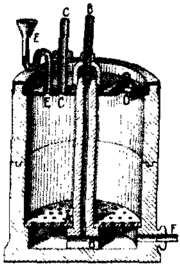

FIG. 5.—Chlorine Still.

HCl	Cl_2 (*free*)	$AlCl_3$	$FeCl_3$	$MnCl_2$	Water
0·7	0·1	0·6	2·8	16·5	73·3 per cent.

It will be observed that even under the ideally perfect conditions represented by the equation, $MnO_2+4HCl=MnCl_2+2H_2O+Cl_2$, only half the chlorine of the acid can be obtained in the free state. The hydrochloric acid consumed by the *impurities in the manganese ore*; *by forms of manganese oxides with a lower power of oxidation than the dioxide*; and the excess hydrochloric acid which escapes oxidation all tend to reduce the efficiency of the process. Various patents have been granted for utilizing the still liquor—*e.g.* it has served for the manufacture of manganese carbonate for purifying coal gas (R. Laming);[10] for deodorizing fæcal matters (J. Dales); for converting barium sulphate to the chloride (F. Kuhlmann); for the manufacture of brown pigments of various kinds by the precipitation of the manganese oxide with lime (C. Crockford); and for the manufacture of pure manganous chloride (K. Muspratt and B. W. Gerland). Various other proposals for utilizing the free acid of the still liquor have been made, and patents have been taken for recovery of manganese dioxide by precipitating manganese oxide with lime and subsequently oxidizing the precipitate with air. None of these processes can be regarded as successful;[11] the recovered manganese in some cases cost more than the original ore, or else it did not work satisfactorily. W. Weldon's improved process is founded on the fact that the freshly precipitated manganese hydroxide suspended in a soln. of calcium chloride, is easily converted into the dioxide when an excess of lime is present. Many of the older processes recovered manganese dioxide by the action of a current of air upon the manganese hydroxide precipitated by lime, but the oxidation is so slow as to be useless in practice, and even then only about half is converted into the peroxide, for the oxidation seems to stop when the manganese is oxidized to the sesquioxide, Mn_2O_3. In **Weldon's recovery process**, it is the excess of lime which led to commercial success, for there is a complete conversion to the dioxide in less than one-tenth the time required for maximum conversion when there is no excess of lime. W. Weldon showed that the complete oxidation of the precipitated manganese hydroxide can take place only in the presence of a strong base. Manganese dioxide has weakly acidic properties, and, in the absence of strong bases, it combines with unchanged manganese oxide, MnO,

to form manganese manganite, $MnO.MnO_2$, *i.e.* Mn_2O_3. If lime is present, the formation of calcium manganite, $CaO.MnO_2$ and $CaO.2MnO_2$, is much faster than the formation of manganese manganite, and all the manganese is then converted to the higher oxide.

The application of Weldon's recovery process involves treating the acid still liquor with ground chalk or limestone to neutralize the free acid and precipitate the oxides of iron. The clarified liquid is run into a tall cylindrical vessel, where it is mixed with milk of lime in sufficient quantity to precipitate all the manganese as manganese hydroxide, $Mn(OH)_2$. The reaction is symbolized: $MnCl_2+Ca(OH)_2=Mn(OH)_2+CaCl_2$. An additional amount of lime—from one-fifth to one-third the quantity previously employed—is introduced; the liquid is warmed to about 55° or 60° by blowing in steam; and air from a compressor is driven through the liquid for about 2½ hours. The manganese is converted into the dioxide, and the contents of the vessel run into a vat, where the manganese dioxide is precipitated as calcium manganite, $CaO.MnO_2$. The reaction is symbolized: $2Mn(OH)_2+2Ca(OH)_2+O_2=2(MnO_2.CaO)+4H_2O$. More still liquor is added and the blowing continued whereby $CaO.MnO_2$ is converted into $CaO.2MnO_2$. The reaction is *represented*: $2MnO_2.CaO+2CaO+2MnCl_2+O_2=2(CaO.2MnO_2)+CaCl_2$. The slurry is run into settlers, where the manganite deposits as a thin mud—Weldon mud. The clear *liquid—largely calcium chloride—is run to waste; no use has been found for but a very* limited quantity of this by-product. The mud is pumped into special chlorine stills where it is mixed with hydrochloric acid. The mixture is warmed by blowing in steam. After the chlorine has ceased to be evolved, the residual liquid is treated as before. The circulation or transport of the liquids and slimes is effected wholly by pumping machinery; the time required for completing one cycle is comparatively short; and the plant is simple and inexpensive. These advantages secured an unprecedented success for this process of manufacturing chlorine.[14]

The theory of the process is incomplete, but that outlined above, based on the acidic qualities of manganese dioxide, is due to W. Weldon.[13] It will be observed that Weldon's mud has a composition approximating to $CaO.2MnO_2$, and, in the chlorine still, this reacts: $CaO.2MnO_2+10HCl=CaCl_2+2MnCl_2+2Cl_2+5H_2O$; if manganese sesquioxide were used: $Mn_2O_3+6HCl=2MnCl_2+3H_2O+Cl_2$. The consumption of acid per unit of chlorine, as well as the reduction in the time required for the oxidation is therefore in favour of Weldon's process. It is, however, a blemish that it produces less chlorine per unit of acid than native manganese ore of good quality; and, as W. Weldon himself has said, it is a barbarous process that yields only *one-third of the total chlorine of the acid treated*, and that the other two-thirds are wasted as calcium chloride.

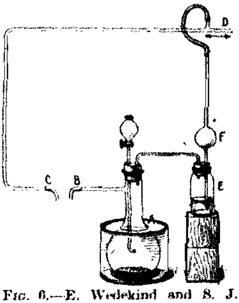

Fig. 6.—E. Wedekind and S. J. Lewis' Chlorine Generator.

2. *The oxidation of hydrochloric acid by potassium permanganate.*—H. B. Condy [14] obtained a provisional patent for the preparation of chlorine by heating a mixture of sodium chloride, sodium permanganate, and sulphuric acid. The process was to be used when a fairly pure product was required for manufacturing purposes. C. M. T. du Motay developed a process in which hydrochloric acid is passed over a heated mixture of lime and potassium permanganate. This salt is a very convenient oxidizing agent for preparing chlorine on a small scale, at ordinary temp. A flask containing some crystals of potassium permanganate—say 10 grms.—is fitted as indicated in Fig. 4 and connected with a wash-bottle containing conc. sulphuric acid. Dilute hydrochloric acid—60 to 65 c.c. of acid of sp. gr. 1·17—is run, drop by drop, from a tap funnel, when chlorine is evolved by the reaction: $2KMnO_4+16HCl \rightarrow 8H_2O+2KCl+2MnCl_2+5Cl_2$. S. J. Lewis and E. Wedekind's [15] apparatus is illustrated in Fig. 6.

The apparatus, Fig. 6, is intended to furnish a regular supply of gas under control. The permanganate is placed in the flask *A* furnished with a stoppered funnel from which

the supply of acid is regulated. The gas passes through the exit tube *B*, where it is to be used, and any excess escapes *viâ* *C*, *D* to the outside air. The bottle *E* contains water or sulphuric acid, and it acts as a safety tube. If the pipette *F* be lifted above the surface of the liquid in *E*, the gas will escape through *F* and *D* into the outside air. When the supply of acid is cut off, the evolution of gas ceases when all the acid is used up.

According to A. Scott,[16] potassium permanganate is very liable to be contaminated with chlorates which introduce chlorine oxides into the gas. The only safe test for these impurities is to absorb the gas in a neutral soln. of potassium iodide, and just decolorize the soln. with sodium thiosulphate. If the addition of pure dilute hydrochloric acid does not restore the blue colour, the absence of chlorine oxides may be inferred: $3Cl_2O+7KI=3I_2+KIO_3+6KCl$, and $6ClO_2+10KI=3I_2+4KIO_3+6KCl$. The hydrochloric acid destroys the iodate: $KIO_3+6HCl+5KI=6KCl+3H_2O+3I_2$.

3. *The oxidation of hydrochloric acid by chlorates.*—L. von Pebal (1875)[17] and G. Schacherl (1876) have investigated the preparation of chlorine by the action of potassium or sodium chlorate on hot conc. hydrochloric acid. If the temp. is low, the gas will be contaminated with chlorine oxides and oxygen. The reaction is somewhat complex.[18] The two main reactions are: $HClO_3+5HCl\rightarrow 3Cl_2+3H_2O$; and $2HClO_3+2HCl\rightarrow 2ClO_2+Cl_2+2H_2O$. F. A. Gooch and D. A. Kreider recommend washing the gas in a warm soln. of manganous chloride in conc. hydrochloric acid, or better, by passing the gas through a heated tube packed with asbestos. This process offers no advantages over other processes; it is far less convenient; and there is a risk of explosions.

4. *The oxidation of hydrochloric acid by nitric acid.*—C. Watt and T. R. Tebutt[19] proposed to make chlorine by heating lead chloride with nitric acid, but the patent was of no technical importance. C. Dunlop heated a mixture of sodium nitrate and chloride with sulphuric acid, and passed the mixture of chlorine and nitrous gases through conc. sulphuric acid—the chlorine passes on, the nitrous gases are retained by the sulphuric acid. This process was in use at St. Rollox for some years where the chlorine was used for making bleaching powder, the by-product of nitrous vitriol was utilized in the sulphuric acid process. H. Goldschmidt[20] supposed that the reactions furnished nitric and hydrochloric acids—aqua regia, in fact—which decomposed into nitrosyl chloride and chlorine: $3HCl+HNO_3=2H_2O+NOCl+Cl_2$; and in contact with water or sulphuric acid, $NOCl+H_2O=HNO_2+HCl$. These reactions are but approximations to the far more complex changes which actually occur. G. Lunge represents the reaction: $3NaCl+NaNO_3+4H_2SO_4=NOCl+Cl_2+2H_2O+4NaHSO_4$, which corresponds with those of H. Goldschmidt. Many other modifications have been proposed.[21] In T. Schlosing's process, a mixture of nitric and hydrochloric acid reacts with manganese dioxide, chlorine is evolved and manganese nitrate is formed: $MnO_2+2HNO_3+2HCl\rightarrow 2H_2O+Cl_2+Mn(NO_3)_2$. The latter when dried and calcined furnishes manganese dioxide, MnO_2, and nitrous fumes, $Mn(NO_3)_2\rightarrow MnO_2+N_2O_4$, which can be converted into nitric acid; $2N_2O_4+O_2+2H_2O=4HNO_3$. There is a loss of about 10 per cent. of the nitric acid in the working of the process. This process is a variant of a patent by F. A. Gatty in 1857.

5. *The oxidation of hydrochloric acid by chromates or dichromates.*—In 1848 A. MacDougal and H. Rawson[22] patented the manufacture of chlorine by heating chromates or dichromates—preferably those of calcium—with hydrochloric acid, directly or indirectly. The process with potassium dichromate was recommended by E. M. Péligot, J. G. Gentele, and H. E. Roscoe for preparing a fairly pure gas: $K_2Cr_2O_7+14HCl=2CrCl_3+2KCl+7H_2O+3Cl_2$.

6. *The oxidation of hydrochloric acid by bleaching powder.*—Chlorine can be made by the action of an excess of hydrochloric acid on an alkaline hypochlorite or bleaching powder. The process was suggested by M. Boissenot[23] in 1849, and later recommended by A. Mermet and H. Kämmerer. According to C. Winkler, the bleaching powder may be compressed into cubes with suitable binding agent—say plaster of Paris. The gas comes off at ordinary temp., and the cubes used in Kipp's

apparatus with hydrochloric acid of sp. gr. 1·124 dil. with its own volume of water —but no sulphuric acid. According to J. Thiele, no binding agent is necessary.

7. *The catalytic oxidation of hydrochloric acid by atmospheric air.*—R. Oxland,[24] in 1845, patented a process for making chlorine by passing a mixture of hydrogen chloride and air through red-hot pumice and washing out the undecomposed gas by water. Ten years later, H. Vogel proposed to prepare chlorine by heating cupric chloride to dull redness, about 500°, whereby cuprous chloride is formed: $2CuCl_2 = 2CuCl + Cl_2$. The cuprous chloride was then mixed with hydrochloric acid and oxidized by air when he supposed cupric oxychloride, $CuCl_2.2CuO.3H_2O$, was first formed, and then cupric chloride itself, so that the end-product of the reaction is regenerated cupric chloride: $4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O$. Stripped from the accessory reaction, it will be observed that fundamentally the reaction may be symbolized: $4HCl + O_2 = 2Cl_2 + 2H_2O$. In practice on a large scale only one-third of the chlorine of cupric chloride was obtained; the copper chlorides quickly corrode stoneware, firebricks, etc.; the manipulation is dangerous to health; and the cost is high owing to the loss of copper.

Various modifications were proposed by C. P. P. Laurent, F. M. A. de Tregomain, and J. T. A. Mallet, but none were successful until 1868, when H. W. Deacon[25] arranged the reactions so that the process is continuous. In the early process the yield was rather small, but R. Hasenclever[26] obtained better results, introducing the hydrochloric acid in a continuous stream into hot sulphuric acid contained in a series of stoneware vessels, and driving out the hydrochloric acid by a stream of air. Although this added to the cost of the operation, since the sulphuric acid had to be conc. again, the process worked more regularly, and the purification of the hydrochloric acid effected by this treatment has added much to the successful working of Deacon's process. It was also found that with impure gases containing sulphur oxides, arsenic oxide, carbon dioxide, etc., the activity of the catalytic copper is rapidly destroyed.[27]

H. W. Deacon showed that the oxidation of hydrogen in hydrogen chloride can be effected by atm. oxygen, by passing the mixed gases through a tube at a high temp. The action takes place below 400° in the presence of pumice-stone sat. with cuprous chloride—CuCl. The result of the reaction is represented by the equation: $4HCl + O_2 + CuCl = 2H_2O + 2Cl_2 + CuCl$. The cuprous chloride remaining at the end of the reaction has the same composition as at the beginning. It is supposed that the first action results in the formation of a copper oxychloride: $4CuCl + O_2 = 2Cu_2OCl_2$; followed by: $Cu_2OCl_2 + 2HCl = 2CuCl_2 + H_2O$; and finally by: $2CuCl_2 = 2CuCl + Cl_2$. Several other guesses[28] have been made on the nature of the cyclic reactions between the catalytic agent and the reacting gases. Iron, nickel, cerium, and other chlorides can be used in place of copper chloride. H. Ditz and B. M. Margosches[29] have patented the use of the chlorides of the rare earths which occur as a by-product in the manufacture of thoria for gas mantles. The chlorine is necessarily contaminated with undecomposed hydrogen chloride, atmospheric nitrogen, atmospheric oxygen, and steam. The steam and hydrogen chloride can be removed by washing, etc. The chlorine so prepared is used in the manufacture of bleaching powder, where the presence of the impurities does no particular harm.

The reaction can be illustrated by the apparatus shown in Fig. 7. Air is forced from a gas holder through a wash-bottle containing hydrochloric acid, and then through a hot porcelain tube containing pumice-stone impregnated with a soln. of cupric chloride and dried. The chlorine gas obtained at the exit can be collected in the usual manner. It is, of course, mixed with the excess of air, nitrogen, etc.

In the reaction: $4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O$, for equilibrium, $[H_2O]^2.[Cl_2]^2 = K'[HCl]^4.[O_2]$, where K' is the equilibrium constant, and the symbols in brackets represent the concentrations of the reacting substances; if partial press. be used P_1 for the hydrogen chloride; P_2 for the oxygen; p_1 for the chlorine; and p_2 for steam, the

equilibrium conditions are $P_1^2P_2^2=K''p_1^4p_2$, where K'' is constant, and if $K''=K^4$, $P_1^{\frac{1}{2}}.P_2^{\frac{1}{2}}=Kp_1.p_2^{\frac{1}{4}}$. The latter represents the equilibrium condition corresponding with the decomposition of one mol. of hydrogen chloride. Observations showed that a mixture containing 92·7 mol. of oxygen and 100 mol. of hydrogen chloride at 352°, reacts until 86·95 per cent. of the hydrogen chloride is decomposed when the system is in equilibrium. Consequently, the equilibrium mixture at 352° contains 100−86·95=13·05 mol. of hydrogen chloride; ½ of 86·95=43·47 mol. of steam; and 92·7−¼ of 86·95 or 71·0 mol. of oxygen. The total press. of the gases was vertically one atm. and therefore the partial press. of the gases must be proportional to these figures, and their sum must be unity, or the partial press. are: HCl, 0·0763; Cl_2, 0·2542; H_2O, 0·2542; and O_2, 0·4152. From the mass law, therefore

$$K=\frac{P_1^{\frac{1}{2}}P_2^{\frac{1}{2}}}{p_1p_2^{\frac{1}{4}}};\ \text{or, } K=\frac{\sqrt{0·2542}\times\sqrt{0·2542}}{0·0763\times\sqrt[4]{0·4152}}$$

or, $K=4·15$ at 352°. The heat evolved during the reaction $HCl+\frac{1}{4}O_2=\frac{1}{2}H_2O+\frac{1}{2}Cl+6·9$ Cals. G. N. Lewis,[30] assuming that the sp. ht. of the four gases do not

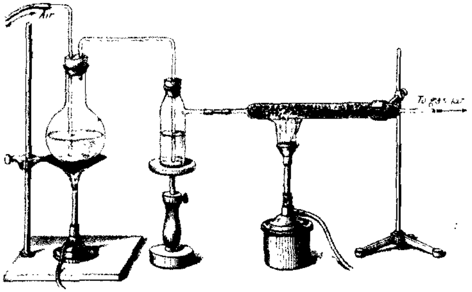

FIG. 7.—Illustration of Deacon's Process for Chlorine.

vary appreciably for temp. ranging between 300°–400°, regarded the heat of the reaction to be independent of the temp. and van't Hoff's equation showing the influence of *temperature* on the reaction, is then represented by $\log K=Q/RT+C'$, where C' is a constant, $R=1·985$, these and $Q=+6·9$. Substituting these values of Q and R, and passing from natural to common logarithms by dividing by 2·3, there follows: $\log_{10} K=1509/T+C$, where C is a constant. Substituting the observed values of K and T, and $\log_{10} 4·15=1509/629+C$, or $C=1·78$. Hence, as a first approximation, the expression $\log_{10} K=1509T^{-1}-1·78$ enables corresponding values of K and T to be computed at 386°, $K=2·94$ (observed) and $K=3·02$ (calculated); at 419°, $K=2·40$ (obs.), 2·35 (calc.). At 25° the computed value of K is 1800. If allowance be made for the variation of the heat of the reaction Q with temp., K. V. von Falckenstein obtains, as a second approximation, $\log K=1437·5T^{-1}-0·534 \log T-0·000021425T+1·7075\times10^{-8}T^2+0·074$. W. D. Treadwell used the expression $\log K_p=6034T^{-1}-6·972$ over the range 300° to 1800°, and the formula is approximately correct down to room temp. The value of K_p at 352° is 2·68; at 600°, −0·06; and at 1984°, −4·30.

The reaction never runs completely to an end, but rather approaches a state of equilibrium: $4HCl+O_2\rightleftharpoons 2Cl_2+2H_2O$, which fixes a definite limit to the yield of chlorine which can be obtained at any particular temperature and concentration of

the reacting gases. The most favourable practical conditions were worked out by G. Lunge and E. Marmier.[31] In the reaction: $4HCl+O_2 \rightarrow 2Cl_2+2H_2O$, 27·6 Cals., both chlorine and oxygen are competing for the hydrogen; at 577° both appear equally strong, for the hydrogen is distributed equally between the chlorine and oxygen. At higher temp. the chlorine is stronger than oxygen, because less free chlorine is obtained than at lower temp., when the affinity of oxygen for the hydrogen is the stronger. In consequence, a greater yield of free chlorine is obtained at temp. lower than 577°. This agrees with the effect of temp. on chemical reactions deduced thermodynamically. Since the reaction is exothermal, the lowering of the temp. favours the formation of chlorine. The temp., however, cannot be reduced indefinitely because the reaction would then become inconveniently slow, even in the presence of the catalytic agent—cuprous chloride. The catalytic agent begins to volatilize at temp. even below 430°. According to K. V. von Falckenstein, the best yield is obtained with a mixture of 40 per cent. HCl and 60 per cent. air, when about 70 per cent. of the hydrogen chloride can be oxidized to chlorine. In accord with the rule that an increase of *pressure* favours the system with the smaller volume, and remembering that over 100°, the system $4HCl+O_2$ occupies five volumes when the system $2H_2O+Cl_2$ occupies three volumes, it follows that an increase of press. should favour the oxidation of hydrogen chloride and augment the yield of chlorine. F. Quincke[32] recommended using oxygen in place of air. This raises the partial press. of the oxygen, and induces a more complete oxidation of the hydrogen chloride to chlorine.

In practice, the mixture of air and hydrogen chloride from the salt-cake gases is driven through cooling pipes and scrubbers to remove moisture, and dried in a sulphuric acid tower. *There are two sets of cylinders heated to about 450° by waste heat.* The cylinders contain broken bricks dipped in a soln. of cupric chloride. The cylinders are recharged about once a fortnight. The exit gases containing 5 to 10 per cent. of chlorine are dried in a sulphuric acid tower and used for making bleaching powder. About two-thirds of the hydrogen chloride is converted into chlorine.

III. The preparation of chlorine by the oxidation of the metal chlorides.—Chlorine can be obtained by the action of oxygen or sulphur upon certain chlorides. The electrical energy required for the electrolysis of the fused chlorides is nearly proportional to their heats of formation—

	$2NaCl$	$CaCl_2$	$MgCl_2$
Heats of formation	195·4	169·8	151·0 Cals.

In the idealized reactions $2MCl+O=M_2O+Cl_2$, where M represents a univalent or an eq. bivalent element, energy respectively eq. to 151·0, 39·0, and 7·0 Cals. per mol. of chlorine is needed. Hence, the manufacture of chlorine by the calcination of magnesium chloride in a current of air appears far more feasible than the treatment of sodium chloride, because the latter requires the expenditure of over twenty times more thermal energy per mol. of chlorine. None the less, patents for the treatment of all these chlorides, and others, have been taken. Thus, W. Longmaid[33] proposes to obtain chlorine by calcining the chlorides of manganese, copper, iron, zinc, or lead with an excess of air. J. Hargreaves and T. Robinson used a mixture of ferric chloride or chlorine oxide and salt; W. Weldon, a mixture of ferrous sulphate and salt; and A. R. Arrott, a mixture of ferrous phosphate and salt. In general, the expulsion of the chlorine may also be facilitated by mixing the sodium chloride with a sulphide, sulphate, silica, boric oxide, stannic oxide, phosphoric oxide, alumina, clay, etc., or a mixture of air with sulphur oxide can be used.[34] Similar remarks apply to calcium chloride. The enormous quantities of calcium chloride produced in the ammonia-soda process has attracted inventors, who have made very persistent efforts to separate the chlorine by a cheap process. Thus, E. Solvay[35] had a series of about twenty patents between 1877 and 1888 directed to the decomposition of the chloride by heating a mixture with sand or clay in a stream of

air. F. Hurtur has shown that the great amount of thermal energy required for the decomposition of sodium and calcium chlorides by chemical process makes it probable that it would be really cheaper to decompose these chlorides by sulphuric acid than by Solvay's process. In an attempt to recover the chlorine from the still-liquor in the manufacture of chlorine from manganese dioxide and hydrochloric acid, W. Weldon [36] mixed the acid liquid with magnesite and heated the dried residue; although the process was not successful industrially, he got the idea [37] that chlorine could be obtained from hydrochloric acid by converting the latter into magnesium chloride: $MgO+2HCl=MgCl_2+H_2O$; and then heating the magnesium chloride in a stream of air: $2MgCl_2+O_2=2MgO+2Cl_2$. The reaction between oxygen and magnesium chloride is reversible,[38] and measurements of the equilibrium conditions when the different reacting members are heated in a closed tube shows that the equilibrium constant K agrees best with the assumption that the reaction proceeds: $2MgCl_2+O_2=2MgO+2Cl_2$, and accordingly $K=C_1^2/C_2$, when C_1 denotes the concentration (partial press.) of the chlorine, and C_2 that of the oxygen. The observed values of K were 0·0324 at 586°; and 0·0625 at 675°. If water vapour be present, equilibrium is established between 350° and 505° through the relation: $MgCl_2+H_2O=MgCl.OH+HCl$; and above 510°, equilibrium is established through the relation: $H_2O+MgCl_2=MgO+2HCl$. Between 505° and 510°, the oxychloride $MgCl.OH$ is decomposed: $MgCl.OH=HCl+MgO$.

Technical details of W. Weldon's process were developed in conjunction with A. R. Péchiney, and the process—called the **Weldon-Péchiney process**—was worked in a continuous cycle of operations: (i) dissolving the magnesia in hydrochloric acid; (ii) mixing the magnesium chloride with a fresh supply of magnesia so as to form magnesium oxychloride, and evaporating to dryness; (iii) breaking, crushing, and sifting the magnesium oxychloride; (iv) heating the magnesium oxychloride to a high temp. when any water present is converted into hydrochloric acid, and the remaining chlorine is given off in a free state; (v) converting the resulting magnesia back to the oxychloride and so on in a continuous cycle of operations. Probably the magnesia acts as a catalytic agent—like copper oxide in Deacon's process—and, in the furnace, converts parts of the hydrogen chloride into chlorine and water. The process was used for a time at Salindres (France), where the mother-liquors from the evaporation of sea-water for salt were treated.

Many modifications have been patented. L. Mond [39] tried to recover the chlorine from the waste liquors of the ammonia-soda process. In **Mond's chlorine process** the ammonium chloride vapour is led over nickel or other metal oxide at about 400°, the chlorine is retained: $NiO+2NH_3+2HCl=NiCl_2+H_2O+2NH_3$, the ammonia passes on. The ammonia gas is then washed out of the apparatus by aspirating an inert gas—producer or flue gas—through the system. If dry air be then led over the nickel chloride at 500°, chlorine is given off: $NiCl_2+O_2=NiO+Cl_2$; and if steam be used, hydrogen chloride is formed: $NiCl_2+H_2O=NiO+2HCl$. L. Mond, however, returned to the use of magnesia in which magnesium oxychloride was produced in place of nickel chloride; and the oxychloride was decomposed by heating in dry air at 800°: $2Mg_2OCl_2+O_2=4MgO+2Cl_2$. The Solvay Process Co. heated mixture of alkali chloride and ferric sulphate in the presence of oxygen.

IV. Electrolytic processes for chlorine and alkaline hydroxides.—In the electrolysis of conc. hydrochloric acid, with carbon or platinum electrodes, chlorine is evolved at the anode, hydrogen at the cathode. When the conc. acid, dil. with eight volumes of water, is electrolyzed, some oxygen is evolved along with the chlorine; with nine volumes of water, still more oxygen is evolved. The more dil. the acid, the greater the amount of oxygen, until, with water acidified with a few drops of acid, no chlorine, but oxygen alone is obtained at the anode.[40] The relation between the yields of chlorine and of oxygen with acids of different concentrations is shown in Fig. 8; with $3N$-HCl, the amount of oxygen obtained was scarcely appreciable. The less the current density the greater the yield of oxygen with soln. more dil. than $\frac{1}{10}N$-HCl; and with more conc. acids, the converse is true.

Other products besides chlorine, hydrogen, and oxygen are obtained. For example, some hypochlorous acid could always be detected in the anode gas obtained in the electrolysis of the more dil. acid; chloric acid accompanied by hydrogen peroxide in small quantities was formed with acids between normal and $\frac{1}{50}N$; and perchloric acid is formed when the more dil. acid is electrolyzed.

If an aq. soln. of potassium or sodium chloride be electrolyzed, chlorine (anion) appears at the anode, and the metal (cation) at the cathode. In the case of sodium chloride, the primary separation is symbolized: $NaCl = Na + Cl - 96{\cdot}4$ Cals. The metal then reacts with the water, liberating hydrogen and forming sodium hydroxide: $2Na + 2H_2O = 2NaOH + H_2 + 86{\cdot}8$ Cals. The thermal energy required to decompose one mol. of sodium chloride and produce a mol. of sodium hydroxide, and a gram-atom each of hydrogen and chlorine is $-96{\cdot}4 + \frac{1}{2}$ of $86{\cdot}8 = -53{\cdot}0$ Cals. The net result of the electrolysis is accordingly symbolized: $NaCl + H_2O = \frac{1}{2}Cl_2 + \frac{1}{2}H_2 + NaOH - 53{\cdot}0$ Cals. Here, 53,000 cals. of thermal energy are eq. to $53{,}000 \div 0{\cdot}24 = 220{,}800$ joules of electrical energy per gram eq.; and since 96,540 coulombs will liberate a gram-eq. of sodium and of chlorine; and electrical energy in joules is equal to the product of the capacity factor in coulombs and intensity factor in volts, $220{,}800 \div 96{,}540 = 2{\cdot}3$ volts are needed to liberate a gram-eq. of sodium and chlorine, on the assumption that the electrical energy is eq. to the thermal value of the reaction. In practice a greater voltage is needed; this is in part due to the expenditure of energy in overcoming the resistance of the electrolyte.

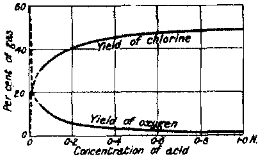

FIG. 8.—Relation between the Yields of Chlorine and Oxygen with Hydrochloric Acid of Different Concentrations.

The probability of manufacturing products by the electrolysis of fused salts was foreseen by M. Faraday[41] in 1834 before the development of the dynamo, which replaced the voltaic battery as a source of electricity on a manufacturing scale.

The capability of decomposing fused chlorides, iodides and other compounds and the opportunity of collecting certain of the products without any loss by the use of simple apparatus, render it probable that the voltaic battery may become a useful and even manufacturing instrument.

The hydrogen gas produced during the electrolysis appears at the cathode and chlorine at the anode. In practice it is found that in the electrolysis of the alkali chlorides, the two electrodes must be separated to prevent the sodium hydroxide formed at the cathode mixing with the chlorine discharged at the anode. There are three main types with many differences in detail.[42]

(1) **Solid diaphragm process.**—A porous diaphragm—Portland cement, earthenware, asbestos, limestone, etc. This permits electrolytic conduction, and greatly retards the mixing of the soln. The *Griesheim cell*[43] is a rectangular steam-jacketed iron box which contains about six cement cases, the walls of which act as diaphragms. Each cement box is provided with an anode made of magnetite, and a lid and exit pipe for the chlorine. The iron box forms the cathode.

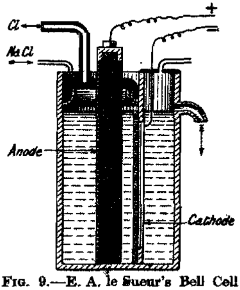

FIG. 9.—E. A. le Sueur's Bell Cell (Diagrammatic).

(2) **Bell process.**—The anode is enclosed in an inverted non-conducting bell with a cathode outside.[44] *E. A. le Sueur's cell* is illustrated diagrammatically in Fig. 9. The electric current flows from anode to cathode. Chlorine gas passes out of the bell, and the

alkali hydroxide forms about the cathode in the compartment outside the bell. The diaphragm is made of asbestos covered with iron gauze which also forms the cathode. Fresh brine flows into the anode compartment through a hole in the lid, and the alkali hydroxide runs from the exit pipe of the outer cell. The electrolyte is always moving from within outwards.

(3) **Mercury cathode process.**—The sodium is dissolved by the mercury to form an amalgam. The amalgam is removed from the cell and treated with water, when sodium hydroxide and mercury are obtained. The mercury is returned to the cell to be used over and over again. In *E. Solvay's cell* (1898),[45] the mercury is circulated through the cell by gravity whence it flows into a separated trough, where it is decomposed by a counter stream of water. The alkaline liquors are drawn off, and the regenerated mercury returns to the cell. The mercury is circulated by an Archimedean screw. In **H. Y. Castner's process** (1893),[46] illustrated in Fig. 10, the reaction between the water and the mercury amalgam takes place in the cell itself. The cell is nearly obsolete, but it illustrates the principle very well.

Each cell has three compartments. The two outer compartments are fitted with graphite anodes (+); and the middle compartment is fitted with an iron grid (−) to serve as cathode. The non-porous partitions do not reach quite to the bottom of the cell but dip into a layer of mercury covering the bottom. A soln. of alkali chloride flows through the two outer cells, and water through the inner compartment. The brine in the outer compartment is decomposed by the electric current into chlorine at the anode and sodium at the cathode. The latter dissolves in the mercury, at the cathode, and the chlorine at the anodes escapes *viâ* the exit pipes. The sodium amalgam diffuses into the inner chamber, and there, coming into contact with the water, is immediately decomposed into sodium hydroxide and mercury. The hydrogen escapes through the loosely fitting cover. The sodium hydroxide is run into a special tank as required. A slow rocking motion is imparted to the cell during the electrolysis, by an eccentric wheel, so as to make the mercury flow from one compartment to the other along the bottom of the cell.

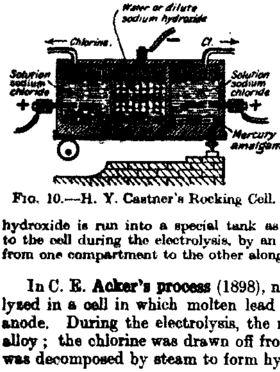

FIG. 10.—H. Y. Castner's Rocking Cell.

In C. E. **Acker's process** (1898), now abandoned,[47] sodium chloride was electrolyzed in a cell in which molten lead was used as cathode, and a carbon rod as anode. During the electrolysis, the molten lead dissolved the sodium forming an alloy; the chlorine was drawn off from the anodes. The alloy of lead and sodium was decomposed by steam to form hydrogen and sodium hydroxide.

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§ 8. The Preparation of Bromine

Bromine is not usually prepared in the laboratory, but if desired it can be liberated from potassium bromide by processes analogous with those employed with sodium chloride, namely, the action of heat on a mixture of manganese dioxide, potassium bromide, and sulphuric acid. Unlike chlorine, the bromine evolved readily condenses to a liquid at ordinary temp. so that in place of a flask, a tubulated retort is employed as illustrated in Fig. 11. In all technical processes the bromine is liberated from its compounds by the action of chlorine, for if chlorine be passed into a liquid containing a bromide until the yellow or reddish colour no longer increases in intensity, the chlorine will have displaced all the bromine: $MgBr_2+Cl_2=MgCl_2+Br_2$. If an excess of chlorine be used, some bromine chloride will be formed. In A. J. Balard's historic process, the liquid was shaken up with ether—or some other suitable solvent, say, chloroform—in a separating funnel; under these conditions, most of the bromine leaves the aq. liquid and collects in the lighter ethereal layer. The lower aq. layer is run off, and an aq. soln. of potassium hydroxide

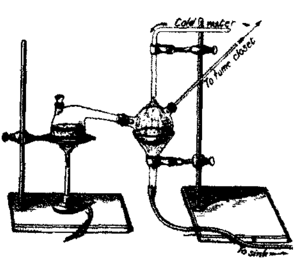

FIG. 11.—The Preparation of Bromine.

is added to the reddish-brown ethereal layer, the bromine forms a mixture of potassium bromide and bromate. The soln. is evaporated to dryness and treated with manganese dioxide and sulphuric acid. This process is too costly on a large scale.

Bromine was formerly obtained from the mother liquid remaining after the separation of sodium chloride from sea-water, a certain proportion of bromine was also extracted from the lixivium of the ash of seaweed, but the proportion in seaweed is small—about one-tenth that of the iodine. The manufacture of bromine from the brine springs of America was commenced at Freeport in 1846 by D. D. Alter; and the manufacture from the saline waters about Stassfurt [1] was commenced in Germany in 1865. The discovery that bromine could be profitably extracted from the Stassfurt salts reduced the price of that element from about 38*s*. 0*d*. to 1*s*. 3*d*. per lb.

About 1837, F. Mohr [2] separated the bromine in the mother liquids of salt springs by treating them with pyrolusite and sulphuric or hydrochloric acid. He showed that at least 5 per cent. of acid must be present or an appreciable amount of bromine will not be formed. The raw material now employed is carnallite, which contains from 0·25 to 0·42 per cent. of bromine. The mother liquid remaining after the separation of the potassium chloride from carnallite contains from about 0·15 to about 0·25 per cent. of bromine in the form of bromocarnallite. In A. Frank's first process [3] the bromine was obtained by mixing the mother liquid with sulphuric acid and manganese dioxide, and heating the mixture by blowing in steam. The mixture of steam, bromine, and chlorine was cooled in a spiral tube. The condensate separated into two layers, a heavy layer of bromine contaminated with chlorine, and a lighter aq. soln. of chlorine and bromine. The latter was added to the next charge in the still, the former was reserved for purification. The fumes from the condenser were passed through a tower packed with iron turnings which arrested the chlorine and bromine. It was found that a considerable loss of time, and of chlorine and bromine were involved in periodically emptying and charging the still. Continuous processes were therefore devised by R. Wünsche and R. Sauerbrey,[4] and K. Kubierschky.

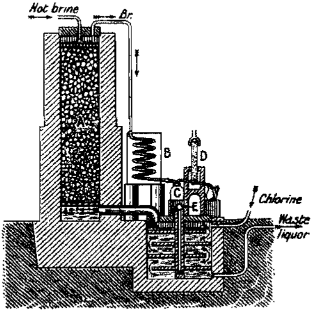

FIG. 12.—Recovery of Bromine from Carnallite Mother-liquors.

The principles of the continuous system are as follows: The hot mother-liquor containing the bromine is allowed to percolate steadily down a tower *A*, Fig. 12, packed with earthenware balls; the descending liquid meets an ascending stream of chlorine gas. The magnesium bromide is decomposed: $MgBr_2+Cl_2=MgCl_2+Br_2$. The excess of chlorine, and the bromine, rising from an exit at the top of the tower, descend, and pass to the condenser where most of the bromine is condensed in a cooled worm-tube, *B*, and collects in the bottle *C*; the uncondensed bromine vapours and chlorine pass into a tower *D* packed with iron turnings kept moist by water. The liquid leaves the base of the tower along the same pipe which brings in the chlorine gas, and runs into a tank beneath the ground. The liquid is forced to flow through this tank to the exit pipe near the bottom in a zig-zag direction. The inflow and outflow of the liquid in this tank is so arranged that the level remains the same. Steam is blown into the liquor *viâ* the pipe *E*. Most of the chlorine and bromine rise to the space above the level of the liquid where they are carried along to the tower with the stream of chlorine from the generator. Waste liquid runs from the underground tank.

The electrolytic processes [5] for separating chlorine from liquors containing

bromides are analogous with those employed for chlorine. The liberated bromine, however, remains in soln., and has to be separated by distillation.

The purification of bromine.—The first product of the extraction contains as impurities,[6] iodine cyanide, carbon bromides, bromoform, and 1 to 4 per cent. of chlorine. This is purified before it is put on the market, and much of the bromine on the market is either free from chlorine or contains at most up to 0·3 per cent. The chlorine is removed by distillation from alkali, calcium, or ferrous bromide.[7] This is the most convenient and effective method of eliminating chlorine. If the bromine is initially very much contaminated with chlorine, a repetition of the treatment after converting the bromine into a bromide may be advisable where a very high degree of purity is desired. S. Piria[8] added baryta water until the bromine is decolorized and evaporated the mixture to dryness. On calcination the organic matter is destroyed, and oxy-halides are transformed into the simple halides. The mass is then treated with sufficient bromine to displace iodine from iodides and again evaporated to dryness and calcined. The remaining mixture of barium chloride and bromide was leached with alcohol, which is said to dissolve the bromide and leave the chloride undissolved. The bromine is recovered from the bromide by heating it with manganese dioxide and sulphuric acid. A. A. B. Bussy[9] removed iodine by precipitation as cuprous iodide; A. Adriani, by treatment with starch paste. The most convenient and effective method of removing iodine is that suggested by S. Piria, namely, converting the bromine into a soluble bromide, and boiling the soln. with a little free bromine. A repetition of the treatment is advisable when the bromine is very much contaminated with iodine.

P. C. E. M. Terwogt agitated the bromine with an excess of water for two or three hours, and removed the bromine by means of a separating funnel. The bromine was then mixed with potassium bromide and a little zinc oxide, and distilled. The distillate was collected under water and redistilled. The product was dried by standing over phosphorus pentoxide, and finally distilled once again. J. S. Stas[10] employed a somewhat analogous process in 1881. According to A. Scott, this treatment removes chlorine and iodine but not organic chlorides and iodides; there is also a risk of the zinc oxide contaminating the product with nitric acid owing to the difficulty of purifying zinc oxide free from nitrogen.

A. Scott prepared highly pure bromine by boiling 1500 grms. potassium bromide in an equal weight of water first with a few crystals of potassium metabisulphite and about 5 c.c. of conc. sulphuric acid, then adding 100 c.c. of sat. bromine water, distilling off the excess of bromine, adding another 100 c.c. of bromine water, distilling off once more, and, after neutralization with potassium carbonate, evaporating to dryness. The dried bromide was now fused with potassium dichromate (which had previously been fused) in the proportion of 500 grms. of bromide to 200 grms. of dichromate. This left an excess of bromide sufficient to retain any quantity of chlorine likely to be present. 1050 grms. of the fused mass, broken up into pieces the size of hazel nuts, were now treated with a *cold* mixture of 450 c.c. of conc. sulphuric acid with 700 c.c. of water. Any organic matter in this mixture was destroyed by adding a small quantity of potassium permanganate. The above quantities gave about 470 grms. of bromine, and on the addition of an excess of dichromate a further 30 grms. of bromine were obtained, which ought to contain all the chlorine. The purified bromine was dissolved in a soln. of potassium bromide—freed from iodine—and distilled.

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§ 9. The Preparation of Iodine

Iodine is displaced from the iodides by any one of the other three halogens—fluorine, chlorine, or bromine. If an excess be used, a compound of iodine with the halogen may be formed. Iodine can be obtained from iodides by a process analogous to that employed for chlorine from chlorides and bromine from bromides, namely, by heating the iodides with manganese dioxide and sulphuric acid: $2KI+MnO_2+2H_2SO_4=K_2SO_4+MnSO_4+2H_2O+I_2$. The iodine vapour condenses in the cooler part of the retort in almost black crystals. Some potassium bisulphate, $KHSO_4$, as well as the normal sulphate, K_2SO_4, is formed at the same time. The direct action of nitric acid or conc. sulphuric acid also liberates iodine from iodides. In symbols: $3H_2SO_4+2KI=2KHSO_4+2H_2O+SO_2+I_2$, in the latter case, and $4HNO_3+2KI=2KNO_3+2NO_2+2H_2O+I_2$ *in the latter*. Various oxidizing agents also liberate iodine from the iodides—thus, with ferric chloride, $FeCl_3$, the reaction is symbolized: $2KI+2FeCl_3=2KCl+2FeCl_2+I_2$.

Most of the iodine of commerce is derived from the ashes of certain varieties of seaweed, or from the mother-liquor—*aqua vieja*—remaining after the extraction of sodium nitrate from the caliche of Chili. Methods have been also proposed for extracting iodine from blast furnace gases,[1] from natural waters,[2] and from natural phosphates;[3] but they have not proved to be of any commercial importance in view of the relative abundance of the Chilian supply. Not much progress has been made by electrolytic processes. T. Parker and A. E. Robinson[4] proposed to electroylze a soln. of the alkali iodide acidified with sulphuric acid, in a cell with a diaphragm separating the platinum or carbon anode from the iron cathode. The iodine which separated at the anode was to be washed with water, and dried by hot air.

Formerly all the iodine was made from the ash of seaweed, and potash was a remunerative appendix to the iodine industry; but just as the Stassfurt salts killed those industries which extracted potash from other sources, so did the separation of iodine from the caliche mother-liquors threaten the industrial extraction of iodine from seaweed with extinction. Iodine in a very crude form was exported from Chili in 1874—*e.g.* a sample was reported with iodine 52·5 per cent.; iodine chloride, 3·3; sodium iodate, 1·3; potassium and sodium nitrate and sulphate, 15·9; magnesium chloride, 0·4; insoluble matter, 1·5; water, 25·2 per cent. About that time much of the iodine was imported as cuprous iodide. This rendered necessary the purification of the Chilian product; but now the iodine is purified in Chili before it is exported. The capacity of the Chilian nitre works for the extraction of iodine is greater than the world's demand. It is said that the existing Chilian factories could produce about 5100 tons of iodine per annum whereas the

world's annual consumption is about 500 tons.[5] In order to prevent the cutting of prices by competition, the Chilian manufacturers have combined to restrict the output, and keep the supply as nearly as possible equal to the demand. As a result, a definite maximum is allocated for each works per annum; so that the plant for the extraction of iodine in any particular works is rarely at work more than a few months each year. A little iodine is yet made from seaweed in Scotland, in Norway, and in Japan.

The extraction of iodine from seaweed.—The deep-sea drift-weed which is washed on to the western coasts of Ireland,[6] Scotland,[7] France, and Norway during the stormy months of spring is collected, dried, and burnt in shallow pits. The product is called **kelp** (formerly *kilpe*, a word of unknown origin) or *varec* or *kelp-ash* in the United Kingdom, and in France, says P. Lebeau,[8] *on le designe parfois sous le nom de kelp ou salin*. On the Normandy coast, the term *varech* is applied generally to the drift-weed or wrack which is thrown on the coast by the sea; and the ash is called kelp or *salin de varech* or *cendres de varech*.

If the drift-weed were to be burnt to a loose ash, it would furnish 25 to 30 lbs. of iodine per ton; in practice, it rarely contains more than 12 lbs. per ton. The low yield is due to faulty treatment in calcination—*e.g.* (i) burning at too high a temp. which causes the volatilization of part of the iodine, and the fusion or fluxing of the ash with sand and pebbles; and (ii) imperfect protection of the kelp-ash from the weather whereby some of the soluble iodides are washed out by rain. High temp. burning also reduces some of the sulphates to sulphides, which later causes a high consumption of acid per unit of iodine.

In 1862, E. C. C. Stanford[9] proposed the carbonization of the drift-weed in closed retorts so as to recover tar and ammoniacal liquor in suitable condensers. This modification did not flourish because of the subsequent difficulties in extracting soluble iodides from the charcoal. V. Vincent (1916) claims that soln. containing aluminium sulphate extract the alkali iodides from seaweed leaving behind the organic matter which prevents the direct precipitation of iodine or iodides. The alkali iodide soln. is treated with copper sulphate for cuprous iodide, or by soln. of sulphites for iodine. M. Paraf and J. A. Wanklyn proposed to heat the drift-weed first with alkali hydroxide so as to form oxalic and acetic acids, which could be crystallized from the lixivium. The economical treatment of seaweed for iodine has been discussed by A. Puge.

E. C. C. Stanford proposed boiling the seaweed with sodium carbonate, the washed residue being termed *algulose*; the acidified filtrate gives a precipitate of what he called *alginic acid* or *insoluble algin*. The filtrate was evaporated to dryness, carbonized, and called kelp substitute; it contains the iodine and potassium salts of the original seaweed. The insoluble algin was converted into the sodium salt and called *algin* or *soluble algin*. Alginates of aluminium, iron, copper, and many other metals are precipitated directly by adding a metallic salt to the soln. of algin. It was further proposed to use alguloso for making a transparent tough paper, and imitations of bone or ivory; algin, as a substitute for gelatine; aluminium alginate in making a waterproof varnish, and as a mordant in dyeing; copper alginate dissolved in ammonia, as a waterproof varnish. The proposals did not prove a commercial success.

The kelp contains 45 to 70 per cent. of soluble salts; 0·5 to 1·3 per cent. of iodine; and 30 to 50 per cent. of insoluble matters. The kelp is extracted with hot water, and the soln. fractionally crystallized; the mother liquid is treated for iodine.

The kelp is crushed into lumps—say, one to two inches diameter—and extracted with water in rectangular iron vats with false bottoms, heated by steam. The liquid of sp. gr. 1·200 to 1·255 is decanted into open iron boiling pans where it is evaporated down to a sp. gr. of 1·325; the salts—mainly potassium sulphate (50–60 per cent.) mixed with sodium sulphate and chloride—which separate by crystallization during the evaporation are removed. The hot liquid is run into cooling vats where crystals of potassium chloride separate. The liquid is again boiled down, and crystals consisting mainly of sodium chloride with 8 to 10 per cent. of sodium carbonate—and called kelp salt—separate from

the hot liquid; the hot liquid, decanted into cooling vats, furnishes crystals containing 80 to 95 per cent. potassium chloride and called *muriate*. These operations are repeated several times. The mother liquid is mixed with about one-seventh its volume of sulphuric acid, free from arsenic; the polysulphides and thiosulphates are decomposed with the separation of sulphur; some hydrogen sulphide and sulphur dioxide is evolved. The liquid is allowed to settle for 24 hrs. in closed lead-lined wooden vats, and decanted for the extraction of iodine. The sediment is steamed for a long time to remove adsorbed iodides. The dried mass—sulphur waste—containing 70 per cent. of sulphur, is used in making sulphuric acid. The sulphate salts are used for manurial purposes in agriculture; the muriate can be used in the manufacture of potash salts; the kelp salt is unsaleable; and the insoluble matter in the lixiviation vats, which consists principally of calcium and magnesium carbonates and phosphates, was once used in making common bottle glass.

Many processes have been proposed for separating the iodide from the mother-liquor resulting from the fractional crystallization of the aq. extract of kelp. A. Payen[10] treated the acidified mother liquid with chlorine, or with potassium chlorate which in conjunction with the hydrochloric acid furnishes chlorine. An excess is avoided or iodine chloride will be formed. The precipitated iodine is washed, dried, and sublimed. Bromine is extracted from the mother liquid by neutralizing the acid, evaporating to dryness, and distillating with pyrolusite and sulphuric acid. F. J. Persoz, L. Boirault, and others have recommended adding copper sulphate mixed with iron filings or ferrous sulphate. The precipitated cuprous iodide, CuI, when heated with manganese dioxide, gives off iodine:

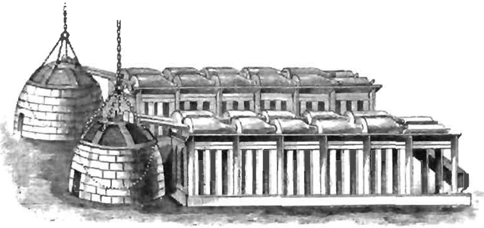

FIG. 13.—Iodine Still with Two Trains of Udell Condensers.

$3MnO_2+2CuI=2CuO+Mn_3O_4+I_2$. T. Schmidt precipitated the iodine as lead iodide, PbI_2. E. Moride precipitated the iodine by treating the liquor with nitric acid; J. Pellieux and M. Launay, used nitrous vapours; R. von Wagner, ferric chloride; M. Luchs, a mixture of potassium dichromate and sulphuric acid; and L. Thiercelin and L. Faure, sulphur dioxide or bisulphites. In the Scottish process, the liquor was heated in stills with sulphuric and manganese dioxide as recommended by W. H. Wollaston, J. J. Berzelius, and others. The iodine sublimes.

Each still consists of an iron pot covered with a leaden lid to which are luted, say, two earthenware arms each of which is connected with a train of about five stoneware aludels or udells supported on a wooden framework as illustrated in Fig. 13. Each udell has a stoneware stopper below so as to permit condensed water (with the 3 halogens in solution) to be drained off as required. Manganese dioxide is added to the liquid. The still is heated by an open fire, and iodine and steam are evolved. The liquor from the still is a troublesome waste product. The udells are emptied when required. The bromine is in too small a quantity to pay to collect. The iodine from the udells requires further purification.

The extraction of iodine from caliche.—The mother-liquor—*aqua vieja*—remaining after the extraction of sodium nitrate from caliche in Chili, contains sodium nitrate, chloride, sulphate, and iodate as well as magnesium sulphate. The iodine content of this liquid amounts up to about 0·3 per cent.; as the original caliche has about 0·02 per cent., the iodine thus accumulates in the mother liquid during the extraction of the nitrate. The mother liquid is run into wooden vats.

and treated with sufficient sodium bisulphate to reduce part of the contained iodic acid to hydriodic acid: $6NaHSO_3+2HIO_3=3Na_2SO_4+3H_2SO_4+2HI$; and to get the right proportion of iodic acid to reduce the remaining hydriodic acid to iodine: $HIO_3+5HI=3H_2O+3I_2$. The soln. is well agitated, and then neutralized with the so-called *sal natron* liquor. After agitation, the liquid is allowed to settle. The iodine is removed, pressed into cakes, dried, and slowly sublimed in cast-iron retorts fitted with udells, as indicated in Fig. 13. The mother-liquor—called *aqua feble*—is returned to the nitrate extraction tanks and is used over again.[11]

The *sal natron* liquor, prepared by heating crude nitrate from the *aqua vieja* tanks with 15 per cent. of coal dust, is made into a cone 5 ft. high with a kind of moat dug round the base of the cone. The cone is sat. with water and ignited. The crude sodium carbonate formed fuses and runs into the pit. The product dissolved in water forms the *sal natron* liquor. The sodium bisulphate soln. is made by passing the fumes of burning sulphur into the *sal natron* liquor. The liquid acid is then acid enough to liberate iodic acid from iodates.

The recovery of iodine from waste liquids.—F. Beilstein[12] recovered iodine from laboratory residues by evaporation to dryness with an excess of sodium carbonate and calcination until the organic matter is all oxidized. The mass is dissolved in sulphuric acid and treated with the nitrous fumes, obtained by treating starch with nitric acid, until all the iodine is precipitated. The iodine is washed in cold water, dried over sulphuric acid, and sublimed. Other oxidizing agents less unpleasant than the nitrous fumes employed by F. Beilstein—*e.g.* hydrogen peroxide—were recommended by G. Torossian for the residues obtained in copper titrations. F. Beilstein's process is applicable to soluble but not to insoluble, oxidized forms of iodine. F. D. Chattaway and K. J. P. Orton found it better to heat on a water bath the waste material, solid or soln., with aqua regia containing a slight excess of hydrochloric acid. This transforms the iodine into iodine chloride. The iodine chloride may be divided into two parts, one half decolorized by the addition of sulphurous acid or a sulphite, and this mixed with the other half. All of the iodine precipitates at once. Iodine chloride may be dil. with an excess water and allowed to stand, when the element separates in long crystals.

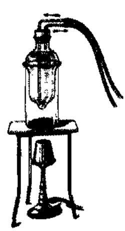

FIG. 14.—Purification of Iodine by Sublimation.

The purification of iodine.—Crude iodine contains from 75 to 90 per cent. of iodine, some iodine chloride, iodine cyanide, water, and different salts. The iodine of commerce is purified by washing it with cold water, drying by press., and subliming from heated iron retorts into udells.[13] The following is a convenient way of purifying small quantities of iodine for analytical purposes:[14]

Grind, say, 6 grms. of commercial iodine with 2 grms. of potassium iodide. Put the dry mixture in a small dry beaker (Fig. 14) fitted with a Göckel's condenser.[15] The beaker is surrounded with a cylindrical asbestos jacket (not shown in the diagram). Place the beaker on a wire gauze, or a hot plate, and heat the apparatus by means of a small flame. The condenser is full of cold water, at the temp. of the room. When violet vapours have ceased to come from the bottom of the beaker, let the apparatus cool. A crust of iodine will be found on the condenser. Pass a current of cold water through the condenser. The glass contracts, and the crust of iodine can be easily removed by pushing it with a glass rod into a similar beaker. The sublimation is repeated without the potassium iodide at as low a temp. as possible. Grind the iodine in an agate mortar, and dry in a desiccator over calcium chloride—not sulphuric acid or the iodine may be contaminated. If the cover of the desiccator is greased, the iodine may attack the grease, forming hydriodic acid, which might contaminate the iodine.

Numerous other modes of purification have been recommended[16] from the simple process of G. S. Sérullas in which the iodine is dissolved in alcohol, the soln. filtered, and the iodine precipitated with an excess of water, to the elaborate process of

J. S. Stas, in which the utmost degree of purity was desired. L. L. de Koninck heated a mixture of potassium iodide with about twice its weight of potassium dichromate; C. Meineke precipitated iodine from a soln. of potassium iodide by the permanganate; and G. P. Baxter converted iodine into hydriodic acid by means of hydrogen sulphide, and after boiling the filtered soln. a few hours to expel hydrogen cyanide, he distilled the iodine with potassium permanganate. Three repetitions of the process gave iodine quite free from cyanides. B. Lean and W. H. Whatmough converted the iodine into cuprous or palladious iodide, and sublimed the iodine by dry distillation of the salt at about 250°. A. Ladenburg precipitated silver iodide from a soln. of potassium iodide; and, after shaking the mixture with aq. ammonia for 24 hrs. to dissolve out the silver chloride, he reduced the silver iodide with zinc and sulphuric acid. The resulting zinc iodide was treated with nitrous acid; the precipitated iodine distilled in a current of steam; and the iodine dried over calcium chloride. M. Baubigny and P. Rivals converted the iodide into iodate by adding potassium permanganate to a soln. of the iodide in sodium carbonate. Five-sixths of the soln. was reduced with neutral sodium sulphite and the iodine was precipitated when the reduced soln. was mixed with the remaining sixth: $5HI+HIO_3=3H_2O+3I_2$. The iodine was filtered, washed, dried, and sublimed. The product was freed from chlorine, bromine, and cyanides. G. P. Baxter oxidized the iodine to iodic acid and recrystallized the latter a number of times from conc. nitric acid. The iodic acid was heated to 100° to drive off moisture, the temp. was then raised to about 240°, and finally heated to 350° in a current of air. The iodide was condensed and finally remelted to remove all traces of moisture. P. Köthner and E. Aeuer found ethyl iodide boiled at 72°, the chloride at about 12°, and the bromide at 38°. Hence, if the halogen is transformed into the ethyl salt, fractional distillation enables the iodide to be separated from the chloride and bromide.

In one of J. S. Stas' processes, the iodine was dissolved in a soln. of potassium iodide. The soln. was diluted with water until a precipitate began to form, and then three-fourths of the amount of water required to precipitate all the iodine were added. The separated iodine was washed free from potassium iodide by decantation, the crystals, after draining, were dried over calcium nitrate in vacuo, and then distilled twice from barium oxide. In another process, J. S. Stas purified the iodine by first treating the iodide with ammonia which converts about 95 per cent. of it into the explosive nitrogen iodide. The washed nitrogen iodide decomposes quietly when warmed with an excess of water. J. S. Stas thus describes the procedure:

Powdered iodine is added to a cold conc. soln. of ammonia in a large flask until the dark brown liquid is nearly colourless. The resulting nitrogen iodide is washed by decantation with cold conc. ammonia until the ammonium iodide is removed. The nitrogen iodide is placed on a funnel with its neck drawn to a fine point, and washed with cold water until the colour of the compound changes to brown, and the wash water is yellowish-brown. The moist iodide is placed in a large glass flask with ten times its weight of water, and slowly heated on a water bath to 60° or 65°. If the temp. be raised above 65°, before decomposition is complete, an explosion may occur. The nitrogen iodide decomposes forming crystals of iodine, a solution of iodine in ammonium iodide, and a white substance—possibly ammonium iodate. When the decomposition appears complete, the liquid is warmed up to 100° for a few minutes. The solid iodine which separates out on cooling is washed with water on a funnel with a drawn-out neck; and afterwards distilled in steam. The iodate is not volatilized. The iodine is dried over calcium nitrate; twice distilled from admixture with about 5 per cent. of finely powdered purified barium oxide; and finally sublimed alone.

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§ 10. The Physical Properties of Chlorine, Bromine, and Iodine

At ordinary temp. fluorine is a gas with a pale canary-yellow colour, chlorine is a gas with a greenish-yellow colour, bromine is a dark reddish-brown liquid which readily forms a reddish-brown vapour when warmed; and iodine is a dark bluish-black crystalline solid which gives a violet-coloured vapour when heated. The colour of the halogen gases is therefore deeper and more inclined to the violet end of the spectrum, the greater the at. wt. The colour of bromine and chlorine gradually becomes paler as the temp. is reduced. At the temp. of liquid air, bromine is pale yellow, chlorine almost colourless. J. H. Kastle[1] tried to show that the characteristic colours of the halogens can be explained on the assumption that the molecules are slightly dissociated even in the solid state, and the observed colour is that of the dissociated halogen. He based his argument mainly on the facts: (1) the colour of the halogens is inversely as their chemical activity; (2) the least stable halogen compounds are the most highly coloured; (3) on heating, the halogen compounds become deeper in tint; (4) the change of colour of bromine on cooling is thus said to be an effect of diminished dissociation (iodine is steel-grey in colour at $-190°$ and at ordinary temp.).

The odour of chlorine is most disagreeable and suffocating; if but small quantities of the gas are present its odour recalls that of seaweed. Chlorine attacks the membrane of the nose, throat and lungs producing irritation, a kind of bronchial coughing, and spitting of blood; the lungs become inflamed, and this is followed by painful death. M. von Pettenkofer and K. B. Lehmann[2] found that 0·001 to 0·005 per cent. of chlorine in the air affected the respiratory organs; 0·04–0·06 produced dangerous symptoms, whilst concentrations exceeding 0·06 per cent. rapidly proved fatal. Bromine like chlorine has a very unpleasant irritating smell; it attacks the eyes very painfully, and is an irritant poison; when in direct contact with the skin it produces troublesome sores. M. von Pettenkofer and K. B. Lehmann add that men cannot stand more than 0·002 to 0·004 per cent. if not habituated; and if habituated, not more than 0·01 per cent. The smell of iodine is not so obtrusive since it is solid at ordinary temp.; it too has a faint smell recalling that of chlorine, but is less unpleasant and less irritating.

The crystalline forms of the halogens.—According to W. Wahl, the crystals of chlorine, bromine, and iodine belong to the rhombic system,[3] and they are isomorphous. The crystals are strongly doubly refracting in sections both parallel and at right angles to the longest axis; and the extinction between crossed nicols is parallel to the longest axis. The optical properties of crystals of bromine are similar to those of chlorine; the crystals have a tendency to develop prismatic forms, and the prismatic cleavages—angle 70°—are very distinct. H. Arctowsky obtained slender carmine-red needle-like crystals of bromine which recall those of chromic anhydride. From B. J. Karsten's and P. C. E. M. Terwogt's observations on the m.p. of the binary systems, Cl-Br, Cl-I, and Br-I, the halogens can form a continuous series of mixed crystals, and they thus appear isomorphous. E. Mitscherlich showed that it crystallizes in the rhombic system with a prism angle of 67° 12′; and E. S. von Federoff found that some crystals on the asbestos stopper of a reagent bottle contained both the ordinary rhombic tablets and prisms belonging to the monoclinic system. Both forms can be obtained from soln. in carbon disulphide, chloroform, petroleum ether, and alcohol. The monoclinic crystals are formed by rapid evaporation, the rhombic form by slow evaporation. V. Kurbatoff found the sublimation of iodine above 46·5° gave the ordinary rhombic crystals, and at lower temp. the monoclinic crystals. Hence, it has been said the iodine is dimorphous with a transition point at 46·5°. W. Wahl could not find a transition point by cooling the ordinary form down to −180°, and considers it is not probable that there is a transition point. He believes that the ordinary form is stable at all temp., and that the monoclinic prisms belong to a monotropic form with a marked temp. limit of formation, and apparently with a low velocity of transformation at ordinary temp.

With chlorine, the polarized light travelling parallel to the cleavage axis is more strongly absorbed, and the transmitted light a deeper yellow with a greenish tint than that passing in directions at right angles to the principal axis. There is a slight difference in the degree of absorption in the two directions at right angles to the principal axis. The crystals of bromine are pleochroic, being dark brownish-red in the direction of the prism axis; yellow-red in the direction of a line bisecting the smaller prism angle; and pale yellowish-green in the direction of the line bisecting the larger prism angle. The change in colour of solid bromine from brownish-red to nearly black at the m.p., and pale yellow at the temp. of liquid air, and to a still paler tint at the temp. of liquid hydrogen, is principally due to a gradual disappearance of the strong trichroism which it preserves near the m.p. The crystals of iodine appear black or light reddish or leather brown according as the polarized light is transmitted with the direction of the principal axis parallel to the plane of polarization, or at right angles to the principal axis. The pleochroism of these three members of the halogen group increases in strength and character as the at. wt. increases—the colour of the strongest absorption in chlorine is the same as the weakest in bromine; and the strongest in bromine, about the same as the weakest in iodine.

The behaviour of the halogens towards the gas laws.—One litre of chlorine gas at 0° and 760 mm., latitude 45°, and at sea-level, weighs 3·1667 grms., when a litre of oxygen under similar conditions weighs 1·42900 grms. The theoretical density with respect to air is 2·4494—under standard conditions. The value observed by J. L. Gay Lussac and L. J. Thénard[4] is 2·47; R. Bunsen, 2·4482; A. Leduc, 2·491; H. Moissan and A. B. du Jassonneix, 2·490 grms. According to E. Ludwig,[5] the vapour density, D, of the gas at a temp. θ° between 0° and 200° is $D=2·4855-0·000178$. According to H. Jahn, above 200°, chlorine follows Boyle's law exactly; M. Pier found that the coeff. of expansion α in the expression $v=v_1(1+\alpha\theta)$ between 0° and 50·24°, $\alpha=0·003873$; between 0° and 100·4°, $\alpha=0·003833$; between 0° and 150·7°, $\alpha=0·003814$; and between 0° and 184°, $\alpha=0·003804$. Similar observations apply to the constant β in the expression $p=p_0(1+\beta\theta)$, which decreases from 0·003807 at 100° to 0·003774 at 184·4°. With rising temp. or decreasing press., the behaviour of chlorine approximates more and more nearly to that of an ideal gas. R. Knietsch's values[6] for J. D. van der Waals' constants are:

$$\left(p+\frac{0·01063}{v^2}\right)(v-0·002050)=RT;$$

and for bromine, $a=0·01434$; $b=0·00202$.

The vapour densities.—The observed densities of chlorine, air unity, are

	0°	100°	200°	0° to 1200°	1400°
Vapour density . . .	2·4910	2·4615	2·4510	2·450	c. 2·02

The ideal value of Cl_2 is 2·4494. The greater density of chlorine below 200° is attributed by M. Pier to polymerization into Cl_4 molecules; and on this assumption he has calculated the degree of dissociation $Cl_4=2Cl_2$, corresponding with the deviations of the observed densities from the ideal value. This assumption is not supported by other evidence, for the molecular condition of liquid chlorine appears to be the same as the gas, Cl_2. The vapour densities of chlorine at high temp., determined by V. Meyer and his co-workers,[7] have a value lower than the normal, and indicate that chlorine is appreciably dissociated into one-atom molecules: $Cl_2=2Cl$, at temp. exceeding 600°, or else that the coeff. of expansion of chlorine is greater than normal. M. Reinganum obtained no evidence of dissociation at 1137° if precautions be taken to prevent errors arising from the tendency of chlorine to diffuse through the walls of the apparatus.

Bromine forms a reddish-brown vapour at ordinary temp. with a vap. press. of 138·1 mm. at 15°, at which temp. E. P. Perman[8] found the vapour density at 15° to be quite normal, but according to H. Jahn, it is rather higher than the normal value 5·5149 if air be unity or 79·92 if oxygen 16 be the unit, for at 102·6° he found 5·7280; at 175·58°, 5·6040; at 227·92°, 5·5243; and he represents the observed vapour density, D, at θ° by the empirical formula $D=5·8691-0·001538$. H. Jahn assumes that the molecules are polymerized at the lower temp. and that with rising temp. or decreasing press., say, by dilution with nitrogen, the density approaches the normal value corresponding with two-atom molecules. At higher temp. the vapour densities are lower than the normal value, and this the more the higher the temp. It is therefore assumed that there is an increasing dissociation: $Br_2\rightleftharpoons 2Br$ with rise of temp.; and calculations from the observed deviations of the vapour density from the ideal value for Br_2 show that the percentage dissociation at

	800°	850°	900°	950°	100°	1050°	1284°
Dissociation . . .	0·16	0·20	1·48	2·53	3·98	6·30	18·3 per cent.

M. Bodenstein and F. Cramer represent the relation between the dissociation and temp. by the formula

$$\log K_p=-10100T^{-1}+1·75\log T-0·0004090T+4·76\times10^{-8}T^2+0·548$$

Similar results have been observed with iodine, but the dissociation [9] is much more marked at even lower temp. The theoretical density for the two-atom molecule is 8·758, air unity; or 126·92 oxygen=16; and for the one-atom molecule the theoretical density is 4·379, air unity. When iodine vapour is heated above 700° its density diminishes steadily up to about 1700°, when it becomes constant at half its value at the lower temp.

Temp.	480°	855°	1043°	1275°	1390°	1468°
Vapour density	8·74	8·07	7·01	5·82	5·27	5·06
Dissociation	0	8·6	25·5	50·5	66·2	73·1 per cent.

Without doubt, the iodine molecule, I_2, dissociates into atoms: $I_2=I+I$. The state of the system in equilibrium will be represented by $kC_{12}=k'C_1^2$. If x denotes the proportion of iodine dissociated, and v the volume of the iodine vapour, then, since v volumes of iodine vapour become $2v$ volumes of dissociated iodine vapour, it follows that the concentration of the dissociated iodine will be x/v, and of the undissociated iodine $(1-x)/v$. Hence for equilibrium

$$k\frac{1-x}{v}=k'\left(\frac{x}{v}\right)^2 \text{ or } K=\frac{k}{k'}=\frac{x^2}{(1-x)v}$$

In every mol. of iodine (I_2) at 1043°, 0·25 mol. will be dissociated; hence, $x^2=0·0625$; $1-x=0·75$; and $K=0·0833/v$. To evaluate v, remember that one mol. of iodine vapour at 0° and 760 mm. occupies 22·3 litres; and at 1043°, 107·5 litres. This quantity of gas contains 0·25 more molecules of iodine because of dissociation, and hence its volume is $107·5+\frac{1}{4}$ of 107·5=134·4 litres. Hence $K=0·0833\div134·4$ $=0·00062$; or $k:k'=0·00062:1$; or 1 : 1600 (nearly). Otherwise expressed, $C_{12}=1600\,C_1^2$, that is, the atoms of iodine will unite 1600 times as fast as the molecules dissociate under such conditions that unit concentration of each is present. The dissociation of iodine molecules is a **unimolecular reaction** because one molecule is concerned in the reaction; and the formation of the two-atom molecule by the union of two one-atom molecules is a bimolecular reaction because two molecules are concerned in the process.

G. Starck and M. Bodenstein represented the relation between the dissociation constant K_p and the absolute temp. T, by the relation $\log_{10} K_p=-7761·96T^{-1}+1·75 \log T-0·00041566T+0·422$, which is closely in accord with observations:

Temp.	1073°	1173°	1273°	1373°	3473° K.
$\log_{10} K_p$ (Observed)	−1·945	−1·325	−0·782	−0·309	−0·091
$\log_{10} K_p$ (Calculated)	−1·956	−1·340	−0·771	−0·311	−0·084

For the sake of comparison, the dissociation constants K of chlorine, bromine, and iodine are respectively 0·01 (1670°), 0·06 (1050°), and 0·66 (1390°). The heat of dissociation $I_2 \rightleftharpoons 2I$, calculated from G. Starck and M. Bodenstein's equilibrium measurements is 35·67 cals. at 1073° K., and 39·64 cals. at 1473° K.; while G. N. Lewis and M. Randall calculate that the increase of free energy in passing from I_2 to 2I is $35650-3·50T \log T+0·0020T^2-1·99T$ cals. I. Langmuir obtained evidence of the formation of *atomic chlorine* by heating chlorine under a low press. by means of a tungsten filament as in the analogous production of atomic hydrogen—*q.v.*

The specific gravities of liquid and solid.—The sp. gr. of liquid chlorine has been determined by R. Knietsch [10] over a range of temp. from −80° to 77°, and A. Lange has also obtained results in close agreement with those of R. Knietsch. The latter represents his sp. gr. D at the temp. θ, by the empirical formula: $D=1·6588346-0·002003753(\theta+80)-0·000004559674(\theta+80)^2$, with a mean error ±0·00148; F. M. G. Johnson and D. McIntosh give the formula $D=1·725$ $-0·00243\ (100+\theta)$. A selection of A. Lange's results for the sp. gr. of liquid chlorine are

	−50°	−40°	−30°	−20°	−10°	0°	10°	20°
Sp. gr.	1·5950	1·5709	1·5468	1·5216	1·4957	1·4485	1·4402	1·4108
	30°	40°	50°	60°	70°	80°	90°	100°
Sp. gr.	1·3799	1·3477	1·3141	1·2789	1·2421	1·2028	1·1602	1·1134

M. Pellaton represented the sp. gr. of liquid chlorine at θ° by the formula $D=0{\cdot}687014+0{\cdot}0002379(144-\theta)+0{\cdot}0622109(144-\theta)^{\frac{1}{3}}$, and for the sat. vapour, $D=0{\cdot}48219+0{\cdot}002451(144-\theta)-0{\cdot}068526(144-\theta)^{\frac{1}{3}}$. *The results are in close agreement with the law of rectilinear diameters. The sp. gr. of liquid chlorine at the b.p. is* 1·568; *and for liquid bromine* according to W. Ramsay and D. O. Masson, 2·9483. The values for the sp. gr. of liquid bromine by the early investigators show considerable variations because the bromine they used was impure and probably contaminated with much chlorine. A. J. Balard's[11] number was 2·966. T. E. Thorpe's number is 3·18828, at 0° water at 4° unity; and 3·15787 at 9·1°. L. W. Andrews and H. A. Carlton give 3·11932 at 20°, 3·10227 at 25°, and 3·08479 at 30°. According to H. Billet, the sp. gr. of liquid iodine at 107° is 4·004; 3·944 at 124·3°; 3·918 at 133·5°; 3·866 at 151·0°; and 3·796 at 170°; and, according to J. Drugman and W. Ramsay, 3·706 at 184·5°. J. Dewar obtained for the sp. gr. of solid iodine, 4·8943 at −38·85; A. Ladenburg, 4·933 at 4°; J. S. Stas, 4·948 at 17°; H. Billet, 4·917 at 40°; 4·886 at 60°; 4·857 at 79·6°; 4·841 at 89·8°; and 4·825 at 107°. G. le Bas estimates the at. vol. of the halogen atoms in combination relative to combined hydrogen, at the critical point, to be

	H	F	Cl	Br	I
Critical temp.	9·7	22·6	58·7	71·6	100·6
	1·0	2·3	6·0	7·7	10·4
B. p.	3·6	8·5	21·7	27·0	37·0

The compressibility coefficients.—The mean compressibility of liquid chlorine at 20° *under the influence of one megabar, i.e.* 0·987 atm., *is* 0·000116 *for press.* between 0 and 100 megabars, and 0·000095 between 100 and 500 megabars; for liquid bromine between 0 and 100 megabars press., 0·0000613, and between 100 and 500 megabars, 0·0000518; for solid iodine, 0·000013 between 100 and 500 megabars press. The compressibility of liquid chlorine, says T. W. Richards,[12] the highest of all the elements, seems to be connected with its large at. vol., its great reactivity, and its volatility, since substances which already possess a large cohesive press. would be naturally less influenced by an external press. The compressibility of solid chlorine is probably less than 50×10^{-6} and may be as low as 25×10^{-6}; and the compressibility of solid bromine is probably less than 30×10^{-6}.

The surface tension.—*The surface tension of liquid chlorine*[13] at −72° is 33·65 dynes per cm., 31·61 at −61·5°; 29·28 at −49·5°; 26·55 at 35·3°; and 25·33 at −28·7. The temp. coeff. of the molecular surface energy is 2·04, very near to the characteristic value for non-associated liquids, and hence it is supposed the molecules of liquid chlorine are present in the state of two-atom molecules, Cl_2. The surface *tension, σ, of liquid bromine*[14] *at θ° is* $\sigma=42{\cdot}00(1-0{\cdot}00381\theta)$ *dynes per cm.* The values observed by W. Ramsay and E. Aston are 40·27 dynes per cm. at 10·6; 34·68 at 46°; and 29·51 at 78·1°. The temp. coeff. agrees with the assumption that the molecules are not more complex than is represented by Br_2. According to R. Schiff, the **atomic cohesion,** a^2, on the assumption that the capillary constant *is an additive quality*, are, in terms of hydrogen unity, 7, 13, and 19 for chlorine, bromine, and iodine respectively.

The viscosity and fluidity.—According to T. Graham,[15] the coeff. of viscosity of chlorine gas is $1{\cdot}287\times10^{-4}$ at 0°, and $1{\cdot}470\times10^{-4}$ at 20°. According to A. Campetti, the viscosity of chlorine is $1{\cdot}328\times10^{-4}$ at 15°, and it is not affected by the arc-light *filtered through a dil. soln. of cupric sulphate to free it from the less refrangible rays.* A. O. Rankine *found* $1{\cdot}297\times10^{-4}$ *at* 12·7°, *and* $1{\cdot}688\times10^{-4}$ *at* 99·1° *for chlorine; and* for bromine, $2{\cdot}48\times10^{-4}$ at 223·4°; $1{\cdot}885\times10^{-4}$ at 99·8°. At T° absolute, the viscosity of bromine vapour is $0{\cdot}00002158T^{\frac{1}{2}}/(1+460T^{-1})$. At the critical temp. the viscosity of chlorine is $1{\cdot}897\times10^{-4}$, and of bromine $2{\cdot}874\times10^{-4}$. According to T. E. Thorpe and J. W. Rodger, the viscosity of liquid bromine is 0·01245 at 0·56°; 0·01035 at 16·16°; 0·00848 at 35·86°; and 0·00706 at 56·48°. According to E. C. Bing-

ham, the fluidity of bromine—*i.e.* the reciprocal of the viscosity—represented by ψ is related with the absolute temp. by the formula $T=0·79098\psi-1376·3\psi^{-1}+227·16$ with an error not exceeding 0·03 per cent. The viscosity of liquid iodine is 2·252 at the m.p. The intrinsic press., K, of the liquid halogens calculated by P. Walden from the relation $K=a/v^2$, where a is van der Waals' constant, and v is the mol. vol. at the b.p.—is 1060 atm. for fluorine, 2135 atm. for chlorine, 2530 atm. for bromine, and 2830 atm. for iodine. The **collision frequency,** 6270×10^6 per second; and the coeff. of condensation from gas to liquid $D_{gas}/D_{liquid}=0·00301$. G. Jäger's[16] estimates of the **molecular diameter** of fluorine, chlorine, bromine, and iodine calculated from the electrical conductivity of salt soln., are respectively 135×10^{-9}, 96×10^{-9}, and 91×10^{-9} cm. The estimates of the diameter of the sphere of action of chlorine based on the kinetic theory of gases furnish numbers ranging from $3·28\times10^{-8}$ to $4·96\times10^{-8}$ cm. A. O. Rankine's estimates, based on the viscosities, are $3·15\times10^{-8}$ cm. for the diameter of the chlorine molecule, and $3·36\times10^{-8}$ cm. for that of bromine; and $1·30\times10^{-22}$ c.c. for the **volume** of the chlorine molecule, and $1·59\times10^{-22}$ c.c. for that of bromine. G. Jäger calculated for the **mean free path** $2·9\times10^{-8}$ cm.—O. E. Meyer gives $4·6\times10^{-6}$ cm.; and for the square root of the mean square of the **molecular velocity,** $3·07\times10^4$ cm. per second; and the arithmetical mean $2·86\times10^4$ cm. per second.

The coefficients of thermal expansion.—The coeff. of cubical expansion of liquid chlorine follows from the determinations of sp. gr. at various temp. According to A. Lange's data,[17] the coeff. of expansion of liquid chlorine, α, is

	−50°	−25°	0°	25°	50°	75°	100°
α .	0·00151	0·00162	0·00187	0·00219	0·00250	0·00314	0·00430

The constant thus increases in magnitude as the temp. rises, until, at about 90°, it is as large as that of the gas. R. Knietsch gave $\alpha=0·001409$ from −30° to 0°, 0·001793 from 50° to 60°; and 0·003460 from 70° to 80°. T. E. Thorpe represents the expansion of liquid bromine at $\theta°$ by the empirical formula $1+0·0010621800\theta+0·0000018771 4\theta^2-0·0000000030 85\theta^3$. J. I. Pierre gave $1+0·001038186255\theta+0·00000171138085 3\theta^2+0·0000000005447118\theta^3$. The constants in the latter formula can be curtailed because after, say, the fourth significant figure the numbers are all out of perspective with the accuracy of the measurements. According to H. Billet, the coeff. of cubical expansion of solid iodine is 0·0002350, and according to J. Dewar 0·0002510 between −38·85° and 17°; the coeff. of thermal expansion for liquid iodine is 0·000856 according to H. Billet.

The liquefaction of chlorine.—The history of the liquefaction of chlorine is interesting. B. Pelletier in 1785 and W. J. G. Karsten in 1786 contested the view that chlorine is a permanent gas because they showed that yellow crystals were formed when the gas is cooled. These crystals were regarded as solid chlorine. In 1810, however, H. Davy[18] showed that these crystals were not formed at −40° F. if dry chlorine be used; that a soln. of chlorine in water freezes more readily than water alone; and that the crystals contain water. He adds: "The mistake seems to have arisen from the exposure of the gas to cold in bottles containing moisture;" and in 1823, M. Faraday showed that what chemists called *solid chlorine* about the end of the eighteenth and beginning of the nineteenth centuries, is chlorine hydrate. On March 5, 1823, M. Faraday was operating with chlorine hydrate in a sealed tube. Dr. J. A. Paris[19] called at the laboratory and noticed some oily matter in the tube Faraday was using; he rallied Faraday "upon the carelessness of employing soiled vessels." Faraday started to open the tube by filing the sealed end; the contents of the tube suddenly exploded; and the "oil" vanished. Faraday repeated the experiment, and Dr. Paris, next morning, received the laconic note:

DEAR SIR,—The *oil* you noticed yesterday turned out to be liquid chlorine.—Yours faithfully, MICHAEL FARADAY.

Chlorine can be condensed to a golden-yellow liquid at 0° and 6 atm. press. By sealing chlorine hydrate in one limb of a Λ-shaped tube, and placing that leg in *warm water while the other leg is immersed in a freezing mixture* (Fig. 15) of, say, *ice and salt, yellow oily drops of liquid chlorine condense in the cold limb.* M. Faraday was much troubled with his *tubes bursting, and refers to the personal damage he sustained in this way.* He speaks of his eyes being filled as with broken glass, and of explosions so violent as to drive pieces of glass through window panes "like pistol shot." M. Faraday was unable to freeze liquid chlorine by cooling it to −40°; but in 1884, K. Olschewsky obtained yellow crystals by cooling the liquid in a bath of evaporating ethylene.

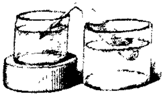

FIG. 15.—Liquefaction of Chlorine.

The critical constants.[20]—For the critical temp. of chlorine, J. Dewar gave 141°; R. Knietsch, 146°; A. Ladenburg, 148°; and M. Pellaton, 144°. The critical temp. of chlorine is about 145°; that of bromine, 302°; and of iodine, 512° (estimated). According to T. Andrews (1871):

If a fine tube be hermetically sealed when one-half of the tube is filled with liquid bromine, and one-half with the vapour of bromine, and gradually heated until the temp. is above the critical point, the whole of the bromine becomes quite opaque, and the tube has the aspect of being filled with a dark red opaque resin. Even liquid bromine transmits much less light when strongly heated in an hermetically sealed tube than in its ordinary state.

R. Knietsch gave for the critical press. of chlorine 93·5 atm., and of bromine, 131 atm. (*estimated*). J. Dewar gave for chlorine, 83·9 atm., and M. Pellaton, 76·1 atm. The critical volume of chlorine is 0·00615, and of bromine, 0·00605. M. Pellaton gave for the critical density of chlorine 0·573.

The boiling and melting points.—H. V. Regnault[21] gave −33·6° at 760 mm. for the **boiling point** of liquid chlorine; and M. Pellaton gave −34·5°. R. Knietsch determined the **vapour pressure** of liquid chlorine at different temp. ranging from −88° to 146°, which latter he regards as the critical temp. For temp. below the b.p., R. Knietsch found the vap. press., in mm. of mercury, to be

	34·4°	−40°	−49·5°	−60°	−66°	−73°	−83°	−88°
Vap. press. .	710	498	365	217	155	100	50	37·5 mm.

and for temp. above the b.p. the vap. press., in atm., were

	−33·6°	0°	20·85°	40°	70°	100°	120°	146°
Vap. press. .	1·00	3·66	6·79	11·5	23·0	41·7	60·4	93·5 atm.

R. Knietsch represents his determinations of the vap. press. p of liquid chlorine at a temp. $\theta°$, between −33·6° and 0°, by the empirical formula: $p=760+32·9127(\theta+33·6)+0·810597(\theta+33·6)^2$ mm.; those between 0° and 40° by $p=2781+82·30166\theta+1·537029\theta^2$ mm.; and those between 40° and 146° by $11·5+0·192966(\theta-40)+0·005365(\theta-40)^2$ atm. M. Pellaton uses $\log p=4·922232-BT^{-1}-C\log T$ atm., where $\log B=2·9676491$; and $\log C=1·8967405$. A. Juliusberger gives $\log_{10} p=4·90847-393·8T^{-1}+0·87093T$ mm. between 185° and 419° K.

For liquid chlorine, M. Pellaton[22] found the value of f in J. D. van der Waals' equation $\log(p_c/p)=f(T_c/T-1)$ is nearly 2·5; the ratio of the critical density to that calculated by the formula of a normal gas $D=Mp_c/22412(1+a\theta_c)$, namely 0·15765; $3·635=D_c/D$; and an application of Trouton's rule, $67·5\times70·92\div238·5$ gives 20·67. Each of these three values is characteristic of what is obtained with non-associated liquids.

The reported b.p.[23] of bromine are very discordant; numbers ranging from 45° to 63° have been given; A. G. Balard's number was 47°. The best representative value is 59° at 760 mm. If extreme trouble is taken to ensure accurate physical

measurements on material which has not been prepared with extreme care so as to ensure the highest degree of purity, the work will be all out of perspective. The bromine of the early observers was, without a doubt, contaminated with x per cent. of chlorine. The vap. press. of liquid bromine in millimetres of mercury are, according to W. Ramsay and S. Young:

	−9·88°	−5·40°	−0·31°	10·4°	28·55°	37·44°	48·7°	56·0°
Vap. press.	38·55	50·9	65·25	111·8	251·0	257·0	540·5	689·0 mm.

H. W. B. Roozeboom's values are a little higher. W. Ramsay and S. Young's and C. and M. Cuthbertson's values for the vap. press. of solid bromine are

	−80°	−63·0°	−46·9°	−28·8°	−14·0°	−12·0°	−8·4°	−7·0
Vap. press.	0·13	0·66	1·83	7·74	25·0	30·0	40·0	45·0 mm.

T. Isnardi observed 65·83 mm. at 0°; 35·37 mm. at −10·9°; 24·95 mm. at −15·5°; and 15·75 mm. at −21·1°. The triple point is −7·3° and 46·4 mm. The vap. press. of solid bromine is given by $\log P = -7109\cdot142T^{-1} - 43\cdot33195 \log T + 133\cdot46929$. The molecular rise of the b.p. of liquid bromine,[24] k, at ordinary press. is 52—the calculated value is 49·5.

Rough estimates of the b.p. of iodine were made by J. L. Gay Lussac,[25] and H. V. Regnault. Later determinations were made by W. Ramsay and S. Young, who found the vap. press. of the liquid, in mm. of mercury, to be

	114·1°	120·4°	127·1°	160·6°	169·4	174·5°	180·75°	184·4°
Vap. press.	80·8	113·4	142·9	475·0	505·5	575·3	680·5	764·2 mm.

J. Dewar represents the vap. press., p, of liquid iodine by the formula: $\log p = 7\cdot924 - 2316T^{-1}$. For solid iodine, G. P. Baxter, C. H. Hickey, and W. C. Holmes, between 0° and 55°, and W. Ramsay and S. Young, between 58·1° and 113·8°, found the vap. press.:

	0°	15°	30°	50°	64·5°	80·4°	102·7°	113·8°
Vap. press.	0·030	0·131	0·469	2·154	6·05	15·15	50·65	87·0 mm.

R. Naumann obtained a vap. press. of 0·00004 atm. at −21°; his other results are lower than those in the above table. J. Dewar[26] represents W. Ramsay and S. Young's vap. press. p of solid iodine between 58·1 and 113·8° by $\log p = 9\cdot3635 - 2872T^{-1}$; and between 85° and 114·1°, by $\log p = 10\cdot0392 - 3137T^{-1}$. W. Nernst represents the vap. press. of solid iodine by the expression $\log p = -3196T^{-1} + 1\cdot75 \log T - 0\cdot003128T + 4\cdot0$, where 4·0 represents the so-called chemical constant of iodine. The formula agrees very well with R. Naumann's measurements.

The **melting point** of chlorine, determined by K. Olschewsky,[27] is −102°. The values for the m.p. of bromine were very discordant before those undertaking the measurement of physical constants realized the vital importance of carefully purifying their materials. The numbers which have been reported range from −7·5° to −25°. A. J. Balard gave −18°. The more recent determinations group themselves about −7·3° as the best representative value for the m.p. of bromine.[28] The m.p. of iodine is 113·6° according to H. V. Regnault; 114° according to W. Ramsay and S. Young; and 116·1° according to A. Ladenberg.[29] A liquid can exist only when the press. is greater than its vap. press.; when the press. is less, the substance can exist only as a gas. If a fusible substance is under a lower press. than corresponds with its vap. press. at the m.p., it cannot melt when heated, but passes at once into the gaseous state—this press. has been called the **critical pressure of the solid.**[30] The principle is readily illustrated by the following experiment:

If a solid piece of mercuric chloride be placed in a glass tube closed at one end and connected with an air pump at the other, it is impossible to melt the salt when the press. is below about 400 mm., however great the temp. applied; the solid merely sublimes. If the press. rises above 450 mm. the solid fuses.

The vap. press. curve of solid iodine is indicated by *PO*, Fig. 16; that of liquid iodine by *OC*; and the effect of press. on the m.p. of iodine by *ON*. At the triple point *O* these curves meet. Fig. 18 shows a similar curve for water. The curve *PO* thus represents the sublimation curve or hoar-frost line; *OC*, the boiling or *vaporization curve, i.e. the effect of press. on the b.p.* of the liquid. The same *phenomenon occurs with water, iodine, etc., and the principle involved is the same as indicated in the law represented by* Clapeyron-Clausius' equations with respect to the lowering of the m.p. by an increase of press. Consequently, if the vap. press. of iodine be less than that of the triple point, the solid does not melt, but rather sublimes directly without melting at the triple point at 114·15° (89·8 mm.) and A. von Richter at 116·1° (90 mm.). According to R. W. Wood, if the **condensation of iodine vapour** occurs above −60°, a black granular deposit is formed, but below that temp. a deep red film is produced.

The melting of bromine or of iodine is attended by an expansion—with bromine, J. I. Pierre[31] found a 6 per cent. expansion. M. Toepler found an expansion of 0·0511 c.c. per gram of bromine, and 0·0434 c.c. per gram of iodine. Hence, by Clausius and Clapeyron's equation the m.p. of bromine is raised 0·0203° per atm. rise of press., and iodine, 0·0314° per atm. rise of press.

The heats of vaporization and fusion.—According to R. Knietsch,[32] the heat of vaporization of liquid chlorine is 67·38 cals. per gram, or 4·78 Cals. per mol. at −22°, and 62·7 cals. per gram at 8°. T. Estreicher and A. Schnerr found at −35·8°, 61·9 cals. per gram or 4·39 Cals. per mol. M. Pellaton gets 64·7 cals. at −22°, and 58·2 cals. at 8°. T. Andrews found the latent heat of vaporization of bromine at its b.p. to be 45·6 cals. per gram, and H. V. Regnault found that 50·95 cals. were involved in condensing to a liquid one gram, of bromine vapour at its b.p. and cooling the liquid to 0°; if the sp. ht. of liquid bromine be 0·108, the heat of vaporization is 44·15 cals. per gram at the b.p. The latent heat of vaporization of solid bromine, according to T. Isnardi, is 60·7 cals. per gram; and for iodine, according to K. Tsurata, 81 cals. per gram; and the mol. ht. of vaporization of liquid iodine is 10·57 Cals., or 10·65 Cals. according to J. Dewar. This is in good agreement with Trouton's rule, as is also the case with bromine and chlorine.

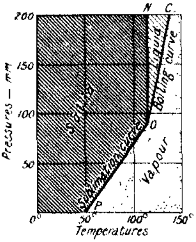

FIG. 16.—Vapour Pressure Curves of Solid and Liquid Iodine.

According to T. Estreicher and M. Staniewsky, the heat of fusion of solid chlorine is, at −108°, 22·96 cals. per gram; H. V. Regnault's value for solid bromine is 16·185 cals. per gram, or 2·6 Cals. per mol. The calculated heat of fusion of iodine is 2·92 cals. per gram, or 3·29 Cals. per mol., and J. Dewar's value for the difference between the observed heats of sublimation and vaporization is 3·78 Cals. per mol. The heat of sublimation of iodine at its m.p. is 14·66 Cals.; J. Dewar gives 14·43 Cals.; R. Naumann, 14·96 Cals.; W. Nernst, 13·94 Cals. at 101°; G. P. Baxter, 15·1 Cals. between 7·5° and 52·5°. The heat of fusion of iodine at 114° is estimated by G. N. Lewis and M. Randall to be 7·27 Cals., and the increase of free energy accompanying the change is $2000-5·17T$, so that at 298° K., the increase in the free energy of iodine in passing from the solid to the liquid state is 4·60 Cals., and in passing from the solid to the gaseous state, at 298° K., 4·64 Cals. G. P. Baxter, C. H. Hickey, and W. C. Holmes found for the increase in free energy in passing from the solid to the gaseous state at $T°$, $16900+6·7T \log T-0·0020T^2-78·73T$; and G. N. Lewis and M. Randall, $26275+1·6T \log T-40·36T$. H. Arctowsky found the speed of sublimation to decrease with increase of press., being twelve times as great at about 16 mm. press. as it is at 760 mm.

The specific heat and thermal conductivity.—A. Campetti[33] found the thermal

conductivity of chlorine gas is about 0·8 times that of air, and it is not altered by the insolation of the gas. The data for the sp. ht. of the halogens are somewhat meagre in comparison with some of the other gases; they suffice, however, to show that the mol. ht. are higher than is usually the case with diatomic gases; and that the ratios of the two sp. ht. are lower. H. V. Regnault's values for the two sp. ht. of gaseous chlorine are C_p=0·1241 and C_v=0·096 between 13° and 202°, hence C_p/C_v=1·291. K. Strecker's values for C_p and C_v are rather smaller, and T. Martini's values smaller still—he gives C_p=0·111; C_v=0·083; C_p/C_v=1·336. The mol. ht. of chlorine, MC_p=8·80 and MC_v=6·81, are higher than is usual for diatomic gases, for which C_p=6·885; MC_v=4·900; MC_p/MC_v=1·41. M. Pier suggests that this is due to the dissociation of imaginary Cl_4 molecules. The phenomenon has been discussed in connection with the sp. ht. of gases. M. Trautz found that the wave length in Kundt's tube alters when the gas is exposed to light; J. W. Mellor could detect no difference.

M. Pier measured the mol. ht. of chlorine, MC_v, at temp. up to 1794°, and found that up to 1400° the results could be represented by MC_v=5·704 ±0·0005 cals., when the corresponding value for normal diatomic gases is MC_v=4·900 ±0·00045 cals. The mol. ht. of chlorine rises from 6·194 at 1288° to 6·317 at 1365°, to 6·677 at 1490°, to 7·600 at 1667°, and to 8·250 at 1894°. It is supposed that the dissociation of chlorine molecules, Cl_2, into atoms, 2Cl, explains the large consumption of heat above 1450°. M. Trautz found that MC_v for chlorine at one atm. press. between 25° and 100° is 5·22; between 25° and 150°, 5·35; and between 25° and 200°, 5·47; and he obtained a smaller value for C_v when the gas is exposed to the light of a quartz lamp. On the contrary, A. Campetti found that illumination made no difference to any of the physical properties he measured.

H. V. Regnault's two values for bromine gas are C_p=0·0555 and 0·05518 between 80° and 230°; and for the mol. ht., MC_p=8·80; MC_v=6·80. K. Strecker found 1·292 for the ratio C_p/C_v between 20° and 388°, where the result is not appreciably affected by temp. changes. Hence K. Strecker gives the values C_p=0·0553 and C_v=0·0428. M. Bodenstein and A. Geiger used the expression MC_p=6·5+0·0064T for the mol. ht., MC_p of bromine gas at the absolute temp. T, but there is a considerable amount of uncertainty about the accuracy of this expression. T. Estreicher and M. Staniewsky found the sp. ht. of bromine between −192° and −80° to be 0·0727 Cal.; and the at. ht., 5·61. K. Strecker's value for the sp. ht. of iodine vapour between 250° and 377° is either C_p=0·0349 or 0·0336, according as the vapour density of iodine be taken as 8·716 or 8·758. The value for C_v is 0·0257, and the ratio of the two sp. ht., C_p/C_v=1·307. The mol. ht. MC_p is accordingly 8·7 between the indicated temp. T. Estreicher and M. Staniewsky found the sp. ht. and at. ht. of iodine between −191° and −80° to be respectively 0·0454 Cal. and 5·76; and between −90° and 17°, respectively 0·04852 Cal. and 6·16.

All the halogens have larger mol. ht. than the usual values for diatomic gases, and this the more the greater the at. wt. of the element. G. Starck and M. Bodenstein represent the mol. ht. at the absolute temp. T, by the empirical formula MC_p=6·5 +0·0038T; and G. N. Lewis and M. Randall provisionally propose 6·5+0·004T for all three halogens.

The sp. ht. of liquid chlorine between 0° and 24° is, according to R. Knietsch,[34] 0·2262; and between −80° and 15°, according to T. Estreicher and M. Staniewsky, 0·2230. H. V. Regnault's value for liquid bromine between 13·21° and 58·36° is 0·11294 cal.; between 11·57° and 48·35°, 0·11094 cal.; and between −6·23° and 10·4°, 0·10513. He also found that the value of this constant decreases as the temp. of the determination is lowered, so that between −7·3° and 10°, the value is 0·106 cal., and between 6° and 14°, 0·108 cal. T. Andrews also obtained the value 0·0171 cal. for liquid bromine between 11° and 45°. According to R. Abegg and F. Halla, the sp. ht. of liquid iodine between 114° and 185°, 0·0630, and the at. ht., 8·01.

The sp. ht. of solid chlorine between −192° and 108°, according to T. Estreicher and M. Staniewsky, is 0·1446, which makes the at. ht. of solid chlorine 5·13. For

solid bromine, H. V. Regnault obtained 0·087 cal. between −77·75° and 0·19°; 0·082 cal. between 7·75° and −22·33°—say, as a mean 0·084. This makes the at. ht. of solid bromine 6·71. H. Barschall found the sp. ht. of solid bromine between −77° and −183° to be 0·073; and F. Koref, 0·075 between −81·1° and −190·8°. From a determination of the sp. ht. of antimony tribromide L. von Pebal and H. Jahn obtained 6·52 for the at. ht. of bromine between 0° and 33°; and 5·67 between −21° and −80°. The sp. ht. of solid iodine between 9° and 98° is 0·05412 according to H. V. Regnault, and W. Nernst found the at. ht. at −244·7°, 3·78; −239·5°, 3·97; −226·5°, 4·17; −196°, 5·38; −87°, 5·92; −38°, 6·36; and at 25°, 6·64.

J. Dewar reported that at −223°, or 50° K.

	Chlorine.	Bromine.	Iodine.
Specific heat . . .	0·0967	0·0453	0·0361
Atomic heat . . .	3·43	3·62	4·59

According to G. N. Lewis and G. E. Gibson,[35] the **entropy** of liquid bromine at 25° is 18·5 per mol., where the increase of entropy in passing from absolute zero to the m.p. T is $\phi=\int C_p d \log T=12\cdot7$; the increase of entropy in passing from the solid to the liquid state at $T°$ K. is 1290/266=4·85; and the increase in passing from the liquid state at 266° K. to that at 298° K. is 0·95. Similarly, the entropy of chlorine gas at 25° is 27·8 per mol., where the increase in passing from absolute zero to the m.p. T of the solid is $\phi=\int C_p d \log T=9\cdot1$; the increase in passing from the solid to the liquid is 817/171=4·77; in passing from the m.p. to the b.p., 2·63; in passing from the liquid to the gas, 10·43; and in passing from the b.p. to 298° K., 0·83. The entropy of iodine at 25° is 15·1 per mol., where the increase of entropy in passing from absolute zero to 298° K. is $\phi=\int C_p d \log T=15\cdot1$. R. C. Tolman's computations yield more than double these values.

G. N. Lewis and M. Randall give for the **free energy** of formation at 25° of solid I, 0 cals., and of solid Br, 157 cals.; of liquid Br, 0 cals.; of liquid I, 460 cals.; of gaseous Br_2, 755 cals.; of gaseous I_2, 460 cals.; of gaseous Br, 22,328 cals.; of gaseous I, 16,965 cals.; of aq. Br_2, 977 cals.; of aq. I_2, 3926 cals.; of a carbon tetrachloride soln. of Br_2, 389 cals. E. Briner estimates the heat of formation $2Cl=Cl_2$ to be 1130 Cals. at 1670°, when the equilibrium constant is 0·01; for bromine $2Br=Br_2+57\cdot0$ Cals. at 1050°—equilibrium constant 0·06; and for iodine $2I=I_2+32\cdot4$ Cals. at 1390°—equilibrium constant 0·66. The ratio of the kinetic energy of translatory motion to the total energy of motion[36] for molecules of gaseous oxygen, nitrogen, hydrogen, and the like is 0·607; for the three halogens this ratio is much smaller, being 0·48 for chlorine, 0·44 for bromine, and 0·46 for iodine.

The refraction coefficients.—The index of refraction of chlorine[37] gas 1·000772 for white light was determined by P. L. Dulong in 1826, and confirmed by M. Croullebois in 1870. The indices for the *C*, *D*, *E*, and *G* lines are 1·000699 (*C*), 1·000773 (*D*), 1·000792 (*E*), and 1·000840 (*G*); and according to C. and M. Cuthbertson for light of wave length ($\mu\mu$)

Wave length .	480·0	520·9	576·9	643·8	670·8$\mu\mu$
Index of refraction .	1·00079166	1·00078651	1·00078135	1·0007703	1·00077563

J. H. Gladstone estimated the refraction eq. of chlorine in its compounds to be 10·05; and later determinations by E. Conrady, J. W. Brühl, and F. Eisenlohr, give for the H- and the Na-lines H_α, 5·933; D, 5·961; H_β, 6·043; H_γ, 6·101. The refraction eq. of the chlorine atom in the acid chlorides is rather higher, *viz.* −6·3 to 6·1. M. Croullebois' value for the dispersion of chlorine $(\mu_G-\mu_C)/(\mu_E-1)$ $=0\cdot1780$; the atomic dispersion $H_\gamma-H_\alpha=0\cdot168$. According to L. Bleekrode, the refractive index of liquid chlorine for the *D*-line is 1·367 at 14°; or 1·385, according to J. Dechant, with a variation of 0·00098 per 1°. This gives for the specific refraction of the liquid by the μ-formula 0·27, and by the μ^2-formula, 0·169; and for the gas respectively 0·24 and 0·16.

The index of refraction of bromine gas at 0° and 760 mm. for the *D*-line is 1·001132 according to E. Mascart. The atomic refraction of liquid bromine, according to J. H. Gladstone, is 15·3; and, according to J. W. Brühl, 8·455 by the μ^2-formula. The specific refraction, according to A. Haagen, is 0·1918. The refractive indices of liquid bromine, selected from measurements by C. Rivière, for rays of different wave lengths, at different temp. as indicated in Table I. These data show that the

TABLE I.—REFRACTIVE INDICES OF LIQUID BROMINE.

Wave length.	Index of refraction.			
	10°	15°	20°	25°
790·9	1·6368	1·6327	1·6280	1·6226
758·6 (*A*-line) . .	1·6394	1·6352	1·6305	1·6250
701·7	1·6453	1·6408	1·6358	1·6304
670·8 (Li-line) . .	1·6495	1·6447	1 6397	1·6343
631·5	1·6557	—	—	1·6401
592·5	—	—	—	1·6475
539·0 (D_2-line) . .	—	—	1·6543	1·6483

refractive index of the liquid is greater the greater the wave length, and the lower the temp. At 20°, the dispersion between the *A*- and *D*-lines is 0·037, which is greater than the corresponding value for carbon disulphide.

The refractive index of iodine vapour for the red and violet lines from a cadmium electrode is 1·00205 for the red, 1·00192 for the violet at 10°; C. and M. Cuthbertson give for light of different wave lengths ($\mu\mu$),

Wave length . .	670·8	621·5	560·0	510·0	500$\mu\mu$
Index of refraction .	1·001970	1·002130	1·002170	1·002210	1·002120

According to F. P. le Roux, like all vapours with a large selective absorption, iodine has an anomalous dispersion since it increases with a fall of temp., being about 0·06 from A. Hurion's measurements—approximately as large a negative number as glass is positive. The atomic refraction of solid iodine is 24·5 by the μ-formula, and 14·12 by the μ^2-formula.

The refractivities of the four halogens—*i.e.* the refractive index less unity multiplied by 10^6—are F, 195; Cl, 768; Br, 1125; I, 1920 (violet) and 2050 (red). According to C. Cuthbertson and E. B. R. Prideaux, if referred to fluorine unity, these constants are nearly in the ratio 1 : 4 : 6 : 10. A similar ratio occurs with neon, argon, krypton, and xenon.

What C. and M. Cuthbertson call the dispersion, $(\mu-1)10^6$, for light of different wave lengths, is 775·63 for chlorine gas for light of wave length 670·8$\mu\mu$; 784·00 for 546·1$\mu\mu$; and 791·66 for 480·0$\mu\mu$; or $\mu-1=7{\cdot}313\times1027/(9629{\cdot}4\times10^2-n^2)$. For bromine gas, the dispersion is 1152·5 for 670·8$\mu\mu$; 1174·1 for 575·0$\mu\mu$; and 1184·9 for 546·1$\mu\mu$ or $\mu-1=4{\cdot}2838\times10^{27}/(3919{\cdot}2\times10^{27}-n^2)$; and for iodine gas, 1970 for 670·8$\mu\mu$; 2130 for 618·0$\mu\mu$; and 2120 for 500·0$\mu\mu$.

The spectra of the halogens.—In 1865, D. Forbes [38] showed that chlorine colours a flame of a Bunsen burner or of a spirit lamp, green; so do chlorine compounds after they have been treated with sulphuric acid. The line spectrum of the halogens obtained by the electric spark has been measured by J. Plücker and W. Hittorf, G. Salet, A. J. Angström, and J. M. Eder and E. Valenta. Most of the lines in the spark spectrum of chlorine fall between 27·6 and 675·8$\mu\mu$, but the majority are at the violet end of the spectrum. The spectrum of chlorine has been more particularly studied by J. M. Eder and E. Valenta, who recorded about 400 lines, most of which were in the ultraviolet, although some extended into the blue, green, yellow, and red. Those in the violet and ultraviolet are sharper than those in the green or yellow,

which latter are, for the most part, broad or indistinct. The line spectrum of chlorine can be observed by the discharge in a vacuum tube containing chlorine at 50 to 100 mm. press.; by sparking the gas at ordinary press.; and from fused chlorides, or minerals containing chlorine. The most pronounced lines of chlorine are the four in the yellowish-green; a bright green line, and a group of lines—three of which are very bright—in the blue. The bromine spectrum is still richer in lines than that of chlorine—the brightest are a group in the blue and one group in the green. The spectrum of iodine in turn is richer in lines than that of bromine—the brightest are a group in the yellow, and a group in the green; there are also many blue lines. If the intensity of a spectral line be represented by its vertical distance from a datum line, the chief spectral lines of the three halogens can be represented as in Fig. 17. Each of the halogens gives two emission spectra—one with the continuous discharge, and the other with the oscillatory discharge. With iodine, if any of the solid be present in the tube during the oscillatory discharge, the vap. press. is so soon altered by the heat of the discharge; as a result, the discharge is damped and the non-oscillatory discharge appears. Hence, with iodine, the oscillatory discharge can be obtained only for a few minutes. G. L. Ciamician specially studied the successive changes which variations of press. have upon the spectra of the halogens. He found that lines which are visible under one press. vanish at another press., because,

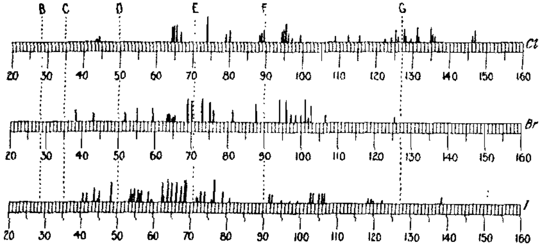

FIG. 17.—Chief Special Lines of Chlorine, Bromine, and Iodine.

according to A. Schuster, there is "a mixture of several overlapping spectra." In general, an increase of press. increases the intensity of the line spectrum, and causes new lines towards the red to become visible. Bromine and iodine also show line or spark spectra under the same conditions as the chlorine spectrum when the electric discharge in a vacuum tube passes through the vapours of these elements. J. M. Eder and E. Valenta showed that bromine vapour at a low press.—8 to 10 mm.—has a distinct and characteristic line spectrum. If the press. is lowered, the spectrum becomes faint, and the lines are broadened. Besides the line spectrum there is a continuous spectrum in the violet at low press. and still a third spectrum at a press. of 45 mm., which seems to correspond with the normal band spectrum of other elements. The flame of hydrogen containing bromine gives a continuous spectrum, so does bromine vapour heated at low redness in a glass tube.

The sat. vapour of iodine in a layer 0·1 metre thick, is opaque to daylight or to candle-light; the vapour appears at the edges to be blue by transmitted light, black by reflected light; and, according to C. F. Schönbein, it appears to be the blacker the higher the temp., owing to an increasing absorptive power for light. C. S. Sellak says that a thin layer of solid or molten iodine transmits only the rays in the extreme red. The fine purple colour of iodine vapour is due to its transmitting freely the blue and red rays of the spectrum, while it absorbs nearly all the green; but if the iodine vapour is in thick layers it absorbs the red rays, and the trans-

mitted light is purely blue. A soln. of iodine in carbon disulphide exhibits the same phenomena since it appears blue or purple according to its density. The red alcoholic soln. does not show this phenomenon. The spark spectrum of a trace of iodine vapour in a vacuum tube shows bright characteristic lines. This spectrum does not correspond with the absorption spectrum; but, according to G. Salet, if a low-tension current is passed through a vacuum tube containing iodine, the spectrum shows a set of bands identical in position with the absorption spectrum of R. T. Thalen.

The absorption or band spectrum of chlorine was examined by W. A. Miller in 1845 and E. Robiquet in 1859, but they failed to detect a line absorption spectrum with chlorine, although one had been previously noted by W. A. Miller in 1833 with bromine and with iodine. A. Morren (1869) and D. Gernez (1872) obtained the desired line spectrum by using a long tube—say, 2 metres in length—filled with the gas. G. D. Liveing and J. Dewar found that a small quantity of chlorine gave a wide absorption band stretching in the ultraviolet from 356 to 302$\mu\mu$, which widened as the amount of chlorine was increased until they obtained a band stretching from 465 to 263$\mu\mu$ (Fig. 18). J. Tyndall found that with the exception of air, nitrogen, and hydrogen, chlorine gas absorbed the long heat rays less than any gas he tried, while K. Angström and W. Palmaer found a single band in the infra-red spectrum stretching from 323 to 607$\mu\mu$ with a maximum at 428$\mu\mu$; E. R. Laird measured the complete absorption spectrum of chlorine at ordinary temp., and found a very broad total absorption band in the violet region, a line absorption in the blue, green, and yellow, particularly rich in the region between 545 and 480$\mu\mu$, and weakening at both ends. The lines do not coincide with the known lines in the emission or spark spectrum of chlorine, although some lines are nearly coincident. With an increase of press., the absorption band in the violet region broadens out rapidly on the less refrangible side and more slowly on the more refrangible side; a decrease of press. does not break the absorption band into lines. W. W. Coblentz has measured the ultra-red spectrum of thin layers of iodine, and found the vapour to be transparent for a wave-length 2·74μ; and with thicker layers the absorption between 1·2μ and 2·7μ is constant. W. Burmeister found no infra-red absorption bands in the absorption spectra of chlorine and bromine. According to R. W. Wood (1896), when iodine (or bromine) vapour is mixed with the vapours of carbon disulphide, a portion of the iodine (or bromine) exists in a state of soln., and gives an absorption spectrum devoid of lines or bands, while another portion exists in the state of a gas, and gives a fine-line absorption spectrum. With a given density of the vapour of the solvent, a portion of the halogen can be vaporized without its showing the gas absorption spectrum, but if a little more halogen be vaporized, the fine lines of the gas absorption spectrum of iodine appear.

The absorption spectrum of liquid chlorine is quite different from that of the gas. C. Gränge found an absorption in the extreme red down to about 697 or 686$\mu\mu$, and from there to about 512$\mu\mu$ red, orange, yellow, and green light is transmitted; absorption begins at 512$\mu\mu$, and is complete in the blue and violet at 503$\mu\mu$. Bromine and iodine vapours like chlorine show a characteristic absorption spectra with many lines. With decreasing atomic weight, an increasing amount of gas must be used to render the absorption lines visible and distinct. Thus, B. Hasselberg required a column of iodine 10 cm. thick, bromine 75 cm., and chlorine 137 cm. to show the absorption lines. The absorption lines shift towards the red with increasing at. wt. This is usually characteristic of the behaviour of the emission spectra of a family group of elements. B. Hasselberg also measured about 3000 lines in the absorption spectrum of iodine, 2500 in the bromine spectrum, and about 1000 in the chlorine spectrum. The number and sharpness of the absorption lines of the halogens thus increase with increasing at. wt. With a higher dispersion, E. R. Laird has shown that the bands of the absorption spectra of iodine and bromine recorded by the early observers are composed of a number of lines. These bands appear as channellings in the spectra and make the spectra appear somewhat similar. Iodine

shows these channellings most distinctly, and bromine and chlorine with diminishing distinctness. The absorption spectrum of iodine and bromine vapours disappears when the dissociation is high, presumably because the monatomic molecules give no absorption in the visible spectrum;[39] the observed absorption spectrum is due to diatomic molecules. The temp. at which the absorption spectrum disappears is higher with bromine than with iodine, and it is augmented by press. R. W. Wood estimated that there are between 40,000 and 50,000 lines in the absorption spectrum of iodine.

G. D. Liveing and J. Dewar found that bromine vapour gives an absorption band

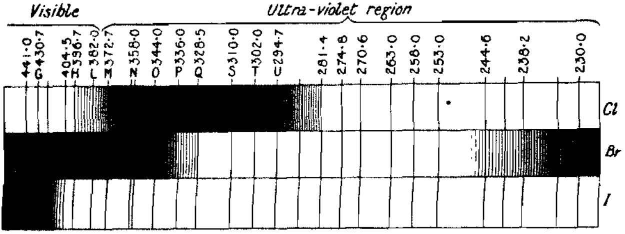

FIG. 18.—Ultraviolet Absorption Spectra of the Halogen Gases.

in the ultraviolet, which begins in the visible spectrum and extends to the solar *L* line, when small quantities of bromine are present, Fig. 18, and to the solar *P*-line when more bromine is present. From this point to the line 250$\mu\mu$, the vapour is transparent, and, after that, the absorption increases with the refrangibility of the rays. C. Ribaud has also studied the ultraviolet spectrum of bromine up to 630°. Thin layers of iodine vapour are transparent for the ultraviolet rays, but there is a strong absorption in the violet region of the visible spectrum; with thicker layers of bromine the absorption extends nearly to the solar *H*-line, Fig. 19, but the vapour is still transparent for rays more refrangible than the *H*-line. The absorption band

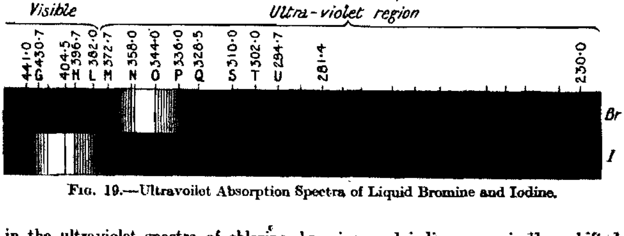

FIG. 19.—Ultravoilet Absorption Spectra of Liquid Bromine and Iodine.

in the ultraviolet spectra of chlorine, bromine, and iodine gases is thus shifted towards the less refrangible or red-end of the spectrum as the at. wt. of the element increases, until with iodine, the absorption band appears in the visible spectrum. A film of liquid bromine between two quartz plates has an absorption band, Fig. 19, which ends just where the transparency of the vapour begins, while the film is opaque for rays above and below this band. With soln. of iodine in carbon disulphide, the spectrum is also transparent for a certain distance, Fig. 18, but is shifted to a less refrangible region lying between the solar *G*- and *H*-lines.

M. de Broglie, working with the zinc compounds of the elements, found the high-frequency spectra of iodine and tellurium to follow one another in accord with their chemical properties; I. Malmer, working with the elements, found that order to be reversed. M. Siegbahn[40] showed that M. de Broglie and I. Malmer used the secondary radiations; and with primary radiations he found the order to be that given by I. Malmer, *viz.* tellurium—iodine. The wave-lengths for the α_1- and β_1-lines agree well with the series:

	Cd	In	Sn	Sb	Te	I	. . .	Ba
At. numbers N .	48	49	50	51	52	53	. . .	56
$\sqrt{\frac{1}{\lambda}}$ α_1 . .	1·304	1·406	1·435	1·461	1·480	1·513	. . .	1·605
$\sqrt{\frac{1}{\lambda}}$ β_1 . .	1·450	1·485	1·521	1·551	1·573	1·606	. . .	1·707

R. W. Wood[41] has shown that if a glass bulb with a few flakes of iodine be exhausted and sealed, a yellowish-green fluorescence appears if a beam of sunlight or arc-light is focussed on the centre of the bulb; if the bulb contains air at atm. press., no fluorescence occurs. Only when the press. is reduced to about 150 mm. does a feeble fluorescence appear. The intensity of the fluorescence gradually increases as the press. is further reduced; the most rapid change occurs when the press. changes from 10 cm. to that of a high vacuum. With hydrogen the fluorescence appears when the press. is about 300 mm. higher than with air. If the bulb is warmed the fluorescence appears at higher press. R. W. Wood explains this by assuming that air at 15 cm. press. is able to dissolve all the iodine which vaporizes at ordinary temp., but by a rise of temp. and consequent increased vapour press. of iodine, some iodine remains undissolved by the air, and it is this portion only which fluoresces. The **fluorescent spectrum** has a number of bands extending from the orange-red into the greenish-blue. R. W. Wood also found that when iodine vapour is heated in a sealed quartz bulb to about 700°, a luminous red cloud is formed—which in thin layers gives a banded spectrum resembling the fluorescent spectrum but displaced a little more towards the red. Heated iodine vapour is probably luminous, as is shown by G. Salet's experiment:

The room was made dark and when a hot glass tube had cooled until it was just barely visible, a fragment of iodine was thrown into the tube, which thereupon filled with luminous vapours. To obtain more brilliancy one heats the vapour of iodine in a Bohemian glass tube by means of an enameller's lamp. The contents of the tube look like a red-hot bar of iron. One may also volatilize iodine around a platinum spiral brought to a vivid incandescence; the luminous vapour rises like a real flame about the spiral. It is a case of *flame without combustion*. The light from the iodine gives a continuous spectrum, or rather a confused primary spectrum; one perceives traces of characteristic channellings but no lines of the secondary spectrum.

J. Evershed, and A. Smithells confirmed and extended these experiments; the former added:

To sum up, then, it appears that besides iodine, the vapours of bromine, chlorine, sulphur, selenium, and arsenic can all be made more or less incandescent by heating to the temp. at which the glass combustion tube softens, and the light emitted by each of these glowing vapours appears to give a perfectly continuous spectrum; while the corresponding absorption spectra are selective. Thus there is no such close relation between emission and absorption as is implied by Kirchhoff's law of radiating bodies. There seems, however, to be a general relation between the total absorbing and radiating power for the visible rays; those vapours which are highly coloured and absorb strongly in the visible spectrum also radiate conspicuously in that part of the spectrum; while colourless, non-absorbing vapours, such as phosphorus, emit no perceptible light when heated.

H. Könen showed that the **thermo-luminescence** of iodine vapour begins at about 550°, and is stronger the denser the vapour, and he adds that the **glow spectrum** of iodine is specially interesting because it is one of the few cases where a visible spectrum is obtained by merely heating a gas. According to W. Friederichs, the banded

absorption spectrum of iodine increases with temp. up to 500°, but decreases at higher temp. until finally it disappears. At 1250°, a continuous emission spectrum was obtained by C. Fredenhagen. Hence it is concluded that the band absorption spectrum is an effect of the diatomic molecules, and becomes weaker as the one-atom molecules begin to form. When a substance is exposed to a beam of radiant energy—say solar light—radiations of a certain wave-length are absorbed, and the energy is expended in inaugurating or stimulating intra-molecular or intra-atomic vibrations. The general effect is to raise the temp. of the body. Waves with a short period of vibration are absorbed, and emitted as heat radiations with a longer period of vibration. There is thus a degradation of radiant energy from waves of a short period to waves of a long period. In the case of fluorescent substances, light waves of short period—e.g. those at the violet end of the spectrum—are absorbed and emitted again as light waves of lower refrangibility.

Violet or ultraviolet radiations may be absorbed and emitted again as green or red rays. This phenomenon is termed *fluorescence* when the *photo-luminescence* is transient and shows only while the body is actually exposed to the light stimulus—e.g. quinine scheelite, fluorspar, uranium glass, barium platino-cyanide, etc.—and *phosphorescence* when the photo-luminescence persists after the stimulant light has ceased to act on the body—e.g. Bologna-stone, Balmain's luminous paint, Canton's phosphorus, and other sulphides of the alkaline earths, some diamonds, etc. G. G. Stokes [42] illustrated the phenomenon by the following simile:

Suppose you had a number of ships at rest on an ocean perfectly calm. Supposing now a series of waves, without any wind, were propagated from a storm at a distance along the ocean; they would agitate the ships, which would move backwards and forwards; but the time of swing of the ship would depend on its natural oscillation, and would not necessarily synchronize with the periodic time of the waves which agitated the ship in the first instance. The ship being thus thrown into a state of agitation would produce waves, which would be propagated from it in all directions. This I conceive to be a rough dynamical illustration of what takes place in this actual phenomenon, namely, that the incidence of ethereal waves causes a certain agitation in the ultimate molecules (or atoms) of the body, and causes them to be in turn centres of agitation to the ether.

In fine, when the ultimate particles of a fluorescent substance are agitated by ether waves from, say, a source of light, they send out fresh waves of their own. The emitted radiations are of shorter wave-length than the absorbed radiations. The rate of transformation of the radiations from a high to a lower refrangibility is rapid with fluorescent substances, and much slower with phosphorescent substances. The absorbed energy may be dispersed in other ways than in developing fluorescent and phosphorescent effects—e.g. it may manifest itself in chemical action—which is utilized in photography; and it may be expended in augmenting the translatory motions of the molecules and be dissipated in the form of heat. In the converse phenomenon, *thermo-luminescence* or *calorescence*, the radiant energy supplied to the body as heat is so transformed that the body becomes luminous in the dark—e.g. some of the green varieties of fluorspar, scheelite, etc.

G. G. Stokes' rule that *the exciting light is of shorter wave-length and greater frequency than that of the excited light* is true only in certain cases. In the case of bodies which do not obey Stokes' law, fluorescence is induced only when the incident light coincides in frequency with one of the sharp absorption bands of the substance, as R. W. Wood showed to be the case with sodium and iodine. P. Lenard's [43] hypothesis assumes that the incident light causes the liberation of electrons from the atoms of the phosphorescent substance, and that light is subsequently emitted when the ejected electrons return to the atoms. This return occupies an appreciable time with substances which have a small electrical conductivity, and, *ex hypothesi*, oppose a great resistance to the motion of the electrons. The return of the ejected electrons is facilitated by a rise of temp. which increases the conductivity. The

theory does not account for the extraordinary influence of extremely small changes in the composition of the phosphorescent substance.

S. Landau and E. Stenz examined the effect of low temp. and dissociation on the fluorescence of iodine vapour at low press. Fluorescence decreases as the temp. is raised, but does not cease at 800°. Dissociation destroys both fluorescence and the resonance spectra. It is therefore inferred that the complex vibrating system is not inherent in the atom, but in the molecule; that the structure of the atom is relatively simple; and that, in all probability, the absorption lines which are so characteristic of diatomic iodine and so sensitive to the action of monochromatic light, do not belong to the absorption spectrum of monatomic iodine.

W. Steubing found that the intensity of the fluorescence of iodine vapour is weakened between the poles of a powerful electromagnet. The result has nothing to do with the Zeeman effect, and has no connection with effects produced by admixture with gases, solvents, etc. It is produced by a direct action of the magnetic field on the electrons causing the band spectrum weakening the individual vibrations.

In 1871, E. Budde [44] showed that when chlorine is exposed to light rays of high refrangibility, an expansion—called the *Budde effect*—occurs and the temp. rises about 1°. This is not a direct heating effect of sunlight since the interposition of a screen between the source of light and the chlorine to cut off the heat rays makes no difference to the effect. A. Richardson showed that the photo-expansion is proportional to the intensity of the more refrangible rays of light. E. Budde suggested that the expansion may be due to the light loosening or actually decomposing some of the chlorine molecules into free atoms, Cl_2 (2 vols.)$\rightleftharpoons$2Cl (4 vols.), and that the slight rise of temp. is developed by the recombination of the *gelockerten und zersetzen Chlormoleküle*. He also showed that the expansion cannot be due to the direct warming effect of sunlight such as occurs, for example, when lampblack is exposed to the red-heat rays, because the red-heat rays are least active in producing the effect. J. W. Mellor showed that the photo-expansion is directly proportional to the rise of temp., and that it is unnecessary to assume that the chlorine molecule is dissociated into atoms when exposed to the actinic rays. The phenomenon is thus analogous with photo-luminescence. In both cases, intramolecular vibrations stimulated by light are degraded into less refrangible vibrations which make themselves evident in the one case by a rise of temp., and in the other case by luminescence. According to M. Trautz, the expansion in light is not the same as when an equivalent amount of heat is applied to the non-illuminated gas. As indicated above, A. Campetti found that ultra-violet light does not appreciably modify the viscosity and thermal conductivity of chlorine gas; and, contrary to M. Trautz's opinion, this light does not affect the sp. ht. at constant vol. According to H. B. Baker and W. A. Shenstone, there is no Budde effect if the chlorine is dry, but it is produced by dry chlorine if platinum be present. In this case the chlorine attacks the platinum in light not in darkness; and in the case of moist chlorine, there is a chemical reaction, $2Cl_2+2H_2O\rightleftharpoons4HCl+O_2$. According to P. Caldwell, the effect does not occur with bromine—if so, it may be that the active rays must be those concerned in that portion of the absorption band of chlorine not covered by that of bromine—Fig. 18.

Electrical properties.—J. J. Thomson (1887) [45] reported that when electric sparks were passed through iodine vapour between 200° and 230°, there was a considerable increase of press. which persisted for some hours. J. J. Thomson attributed this phenomenon to what he estimated as a 47 per cent. dissociation: $I_2=I^{\cdot}+I'$. J. J. Thomson also studied the phenomenon with chlorine. According to E. P. Perman (1891), no perceptible change of density is produced by the discharge; and according to W. Kropp (1915), there is no evidence of such a phenomenon in quartz. J. J. Thomson could not detect the presence of free ions either in the preliminary stage of the insolation of a mixture of hydrogen and chlorine, or in the later stage when the gases are actively combining. The method employed was

sensitive to 1 in 10^{14} of the molecules present. M. le Blanc and M. Vollmer could detect no signs of ionization when the mixture was illuminated by an osram lamp. The fog observed by P. V. Bevan to be produced when a combining mixture of hydrogen and chlorine is expanded is not necessarily due to ionization, for P. Lenard has shown that ionization, the formation of fogs, and chemical action are independent phenomena. G. Kümmell's report that a measurable ionization is produced by the insolation of chlorine, is thought to be based on a mal-observation due to defective insulation. E. Radel found that when moist chlorine is exposed to light from electric sparks repeated every hundredth of a second, a faint cloud can be detected by ultra-microscopic methods. Radiations from polonium or radium bromide act similarly, but the effect is weaker.

J. S. Townsend[46] showed that the chlorine gas liberated by the action of hydrochloric acid on manganese dioxide has a strong positive electrification. The **spark potential,** V, that is, the lowest difference of potential between two electrodes required for sparking, is not constant for chlorine-air, nor for bromine-air.[47] In each case, there is a gradual increase with an increasing sparking distance and an increasing gas press., ultimately approaching a limiting value. The converse phenomenon obtains with helium-air. There is an intense green coloration about the positive electrode with chlorine gas which with lower press. becomes very pale, and it then gives the characteristic spectrum. The falls of potential at the anode are very high with the halogens, presumably because the measurements are obscured by the action of the halogen on the electrodes.[48]

A. L. Hughes and A. A. Dixon give 8·2 volts for the **ionizing potential** of chlorine gas, and 10·0 volts for that of bromine, while the value for chlorine calculated from K. T. Compton's formula $V=0·194(K-1)^{-\frac{1}{2}}$ volt, is 4·94 volts, where K denotes the specific induction capacity, and V the ionizing potential representing the least energy required to ionize the gas by the impact of electrons. The calculated value for fluorine is 9·84 volts. C. G. Found obtained for iodine vapour $V=8·5$ volts. E. B. Ludham found chlorine is not ionized by ultraviolet light which is capable of ionizing air. The fluorescence produced in iodine vapour by light of comparatively long wave-lengths led to experiments on the ionization of iodine vapour by exposure to light. J. Henry, E. Whiddington, and J. Franck and W. Westphal obtained negative results with light deprived of most of the ultraviolet by passage through the glass of the apparatus. The latter, however, found that it is easier to produce a glow discharge in fluorescing iodine vapour than through non-fluorescing vapour; hence it is inferred that less work is required to separate an electron from a molecule of the vapour when it is fluorescing than when it is not.

H. M. Vernon exposed chlorine in an ozone tube to the action of a silent discharge, and obtained no other result than a slight expansion due to the heating effect of the discharge. E. Briner and E. Durand also failed to obtain a contraction—even $\frac{1}{2000}$th volume under similar conditions. According to K. Kellner,[49] when purified and dry bromine is exposed, in double-walled tubes like ozone tubes, to the alternating current of 250,000–300,000 volts of a Tesla transformer, a sulphur yellow crystalline deposit is formed on the walls of the tube, and if small quantities of bromine are used, the whole may be transformed into this product; it is stated that the glass takes no part in the change. In the absence of some confirmatory evidence, it cannot be assumed that the bromine is here polymerized. Liquid chlorine is virtually a non-conductor of electricity; according to F. Linde,[50] the conductivity is smaller than 10^{-16} reciprocal ohms; and according to W. A. Plotnikoff, that of liquid bromine is less than 10^{-8} rec. ohms; and G. N. Lewis and P. Wheeler place the specific conductivity of iodine at about 3×10^{-5}. They also find the conductivity of soln. of potassium iodide in liquid iodine between 120° and 160° is equal to that of the best conducting aq. soln. Solid iodine is a very bad conductor, and like other insulators, it develops electricity by friction.[51] K. Fajans found the **heat of hydration of gaseous ions** to be: Cl′, −23; Br′, −32; I′, −43 kgrm. cals. per gram-ion. P. Lenard, W. Weick, and H. F. Mayer calculate that in soln.:

	F′	Cl′	Br′	I′
Number of mols. of H_2O per ion .	11	6	6	6
Radius of complex	$3\cdot9\times10^{-8}$	$3\cdot2\times10^{-8}$	$3\cdot0\times10^{-8}$	$2\cdot9\times10^{-8}$ cm.

R. Lorenz, and P. Walden estimate the **diameter of ions** of chlorine in aq. soln. to be $2\cdot30\times10^{-8}$ cm. at 18°; of bromine ions, $2\cdot24\times10^{-8}$ cm., and of iodine ions, $2\cdot26\times10^{-8}$; in methyl alcohol soln. at 25°, the numbers are respectively $4\cdot98\times10^{-8}$, $4\cdot78\times10^{-8}$, and $4\cdot84\times10^{-8}$ cm.; the **diameters of the atoms** are respectively $2\cdot33\times10^{-8}$, $2\cdot52\times10^{-8}$, and $2\cdot60\times10^{-8}$ cm.; while the **molecular diameters** of bromine and iodine are respectively $3\cdot42\times10^{-8}$ and $3\cdot76\times10^{-8}$ cm.

From the observations of E. C. Sullivan, A. A. Jakowkin, F. Boericke and F. Haber, M. de K. Thompson [52] computed the electrolytic potentials of the halogens in soln. sat. with them, at 25°, to be −1·643 volts for chlorine; −1·353 volts for bromine; and −0·817 volt for iodine. The e.m.f. of the gas-cell Pt | H | HCl | Cl | Pt in which a hydrogen and a chlorine electrode are immersed in aq. hydrochloric acid should be the same as that required to electrolyze hydrochloric acid of the same concentration if the process were strictly reversible; but the observed results are rather less than the theoretical. The gas-cell has therefore been investigated by F. J. Smale, E. Müller, W. von Beetz, B. O. Pierce, and others. According to E. Müller, the chief sources of error are due to the hydrolysis of chlorine according to A. A. Jakowkin's equation, and to the possible formation of perchlorides. E. Müller found that when measured against the hydrogen electrode, the **electrode potentials** of chlorine against hydrochloric acid in the same soln. are

Concentration of acid.	Observed e.m.f.	E.m.f. corrected for hydrolysis.	Calculated e.m.f. from that of *N*-HCl.
N-HCl	1·366	1·366	—
0·1*N*-HCl	1·485	1·486	1·477
0·01*N*-HCl	1·546	1·599	1·594
0·001*N*-HCl	1·587	1·733	1·712

The correction for the increase of chloride ions due to the hydrolysis of the chlorine has largely eliminated the deviations between the observed and calculated values. G. N. Lewis and F. F. Rupert find for the electrode potential of chlorine against the normal electrode to be −1·0795. F. Dolezalek measured the difference in the e.m.f. of two 5*N*- to 12*N*-hydrochloric acid cells of different strengths by the vap. press. method, and obtained satisfactory results. F. Boericke, G. N. Lewis and H. Storch found for the normal electrode potentials against hydrogen at 25° $Br_{2aq.}$ | HBr | H_2, −1·0872 volts; $Br_{2liquid}$ | HBr | H_2, −1·0661 volts; and Br_{2gas} | HBr | H_2, −1·0824 volts. B. O. Pierce gives for H_2 | $NaBr_{aq.}$ | Br_2, 1·252 volts; for H_2 | $KBr_{aq.}$ | Br_2, 1·253 volts; for O_2 | $KBr_{aq.}$ | Br_2, 0·500 volt; for H_2 | $KI_{aq.}$ | I_2, 0·861 volt; and for O_2 | $KI_{aq.}$ | I_2, 0·057 volt. P. D. Foote and F. L. Mohler estimate the **electro-affinity** of chlorine to be 4·8 volts.

F. Linde [53] found the **dielectric constant** of chlorine at −60°, with a wave-length about 10^4 cm., is 2·15; at −20°, 2·03; at 0°, 1·97; at 10°, 2·08; and from 0° to the critical temp. a decrease of about 0·0044 per degree. For liquid chlorine W. D. Coolidge obtained a dielectric constant of 1·88 (14°) and F. Linde, 1·93 (14°). For bromine at 1° for wave-length of about 10^4 cm., P. Walden found 4·6; and at 23° for a wave-length 84 cm., H. Schlundt found 3·18; with iodine, with a wave-length of 75 cm., W. Schmidt obtained a dielectric constant of 4·00.

Magnetic properties.—Chlorine, bromine, and iodine are diamagnetic.[54] The **magnetic susceptibility** of chlorine at atm. press. and 16° is $-0\cdot50\times10^{-6}$ per unit mass; and at 15°, $0\cdot007\times10^{-1}$ per unit volume; for bromine, the magnetic susceptibility at 18° is $-0\cdot38\times10^{-6}$; at 20°, $0\cdot41\times10^{-6}$ per unit mass, and at 19°, $-1\cdot4\times10^{-6}$ per unit volume. For liquid iodine at 115°, the magnetic susceptibility is $-0\cdot4\times10^{-6}$ and 180°, $-0\cdot3\times10^{-6}$ per unit mass, and for iodine crystals at 10°, $-0\cdot35\times10^{-6}$. The **atomic magnetism** of chlorine in organic derivatives is 282, 249, 218, and 194, according as there are 1, 2, 3, or 4 chlorine atoms per molecule;

with bromine, 113, 374, or 334 according as there are 1, 2, or 3 atoms per molecule; and with iodine, 612 or 577, according as there are 1 or 2 atoms per molecule.

The molecular **rotation of the plane of polarization**[55] of sodium light in an electro-*magnetic field with reference to water unity* is for a 10·1 per cent. soln. of chlorine in carbon tetrachloride 1·344 at 7·6°; and the atomic rotation of chlorine (hydrogen unity) is 1·675; and of bromine, 3·563. In studying the influence of a magnetic field on the optical behaviour of chlorine gas, A. Heurung found no appreciable increase in the region of the absorption for light of wave-length 518 to 640$\mu\mu$. R. W. Wood found that if iodine be placed between the poles of a magnet and parallel rays of arc light be sent through a nicol prism, then through a tube containing iodine vapour, and finally through a second nicol, an intense blaze of emerald-green *light appears when the magnet is excited. R. W. Wood (1906) and A. Heurung* (1911) have measured the spectrum of the green light—several new lines make their appearance—and since the magneto-optical effect cannot be eliminated by the rotation of the analyzer, it is inferred that only a small portion of the light is polarized. The effect on the individual spectrum lines of chlorine could not be detected.

Summary.—The gradation in characters which the halogens show with increasing at. wt. from fluorine to iodine, yields one of the most typical family series of elements. The best representative values of some of the physical constants of the halogens are summarized in Table II. The family relationship of the halogens is illustrated by:—

(1) The *similarity* in the chemical and physical properties of the elements and their corresponding compounds, is such that the properties of any one

TABLE II.—PHYSICAL PROPERTIES OF THE HALOGENS.

	Fluorine.	Chlorine.	Bromine.	Iodine.
At. wt.	19·0	35·46	79·92	126·92
State aggregation (0°)	Gas	Gas	Liquid	Solid
Colour	Pale yellow	Yellowish-green	Brownish-red	Violet
Sp. gr. (liq.)	1·108(−187°)	1·568(−33·6°)	2·9283 (59°)	4·004 (107°)
Sp. vol.	0·9025	0·6635	0·3392	0·2698
At. vol.	17·15	23·52	27·13	34·23
Mol. vol.	34·30	47·04	54·26	68·46
B.p.	−187°	−33·6°	50°	183°
M.p.	−233°	−102°	−7·3°	114°
Critical temp.	—	147	302°	512°
Coeff. expansion	—	0·00187 (0°)	0·00106 (0°)	0·000025 (liq.)
Coeff. compressibility	—	0·00095	0·000052	0·000013
Heat of fusion	—	22·96 cals.	16·185 cals.	2·9 cals.
Heat of vaporization	—	67·38 cals.	45·6 cals.	81 cals.
Sp. ht. (0°)	—	0·2662 (liq.)	0·1071 (liq.)	0·0515 (solid)
Sp. ht. gas, C_p	—	0·1155	0·0553	0·0336
Sp. ht. gas, C_v	—	0·0873	0·0428	0·0257
Ratio γ	—	1·323	1·292	1·307
Refractive index	1·000195	1·000768	1·001125	1·001920
At. dispersion	0·022–0·05	0·50	1·22	3·65
At. refraction	0·941–1·015	10·05	15·3	24·5
Magnet. susceptibility	$-3·45 \times 10^{-6}$	$5·9 \times 10^{-6}$	$-4·1 \times 10^{-6}$	$-3·5 \times 10^{-6}$
Dielectric constant	—	1·97	3·18	4·00

member of the family can be said to summarize or rather to typify the properties of all the other members although fluorine diverges a little in some of its properties.

(2) The *gradual transition* of chemical and physical properties such that if the elements be arranged in order: F, Cl, Br, I, the variation in any particular property in passing from fluorine to iodine nearly always proceeds in the same order, and that is the order of their at. wt.

Similar family characteristics will be found with the chemical properties of the

halogens. Taking almost any property and comparing its magnitude in passing from the element fluorine to iodine, or from the fluorides to the iodides, a similar gradation will be observed: Thus, take the m.p. of the cadmium, calcium, barium, sodium, or potassium salts:

	Fluoride.	Chloride.	Bromide.	Iodide.
Sodium	980	820	765	650
Potassium	885	790	750	705
Calcium	1361	780	760	740
Barium	1280	960	880	740
Cadmium	1000	590	350	1000

The markedly greater jump in passing from the fluorides to chlorides than with the other steps in the case of the earths is supposed to be explained by a difference in constitution. There is also a difficulty with the cadmium halides.

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§ 11. Solutions of Chlorine, Bromine, and Iodine in Water, etc.

Chlorine and bromine are fairly soluble in water; iodine has a low solubility. Early determinations of the solubility of chlorine in water were made by J. L. Gay Lussac[1] in 1839, by J. Pelouze in 1843, and by F. Schönfeld in 1855. They noticed a maximum in the solubility curve in the vicinity of 10°, and at 100° the solubility is nil. Later determinations have been made by H. W. B. Roozeboom in 1885, and by L. W. Winkler in 1907. At temp. below 9·6°, chlorine forms a crystalline hydrate, $Cl_2.8H_2O$; and this corresponds with the maximum in the solubility curve. The solubility curves of the gases chlorine and bromine[2] are indicated in Table III.

TABLE III.—THE SOLUBILITY OF CHLORINE AND BROMINE IN WATER (L. W. WINKLER).

Chlorine.			Bromine.		
Temperature.	Absorption coeff.	Grms. Cl in 100 grms. water 760 mm.	Temperature.	Absorption coeff.	Grms. Br in 100 grms. water 760 mm.
0	4·610	1·46	0	60·5	42·9
3	3·947	1·25	2	54·1	38·3
6	3·441	1·08	4	48·3	34·2
9	3·031	0·96	6	43·3	30·6
9·6	3·095	0·94	8	38·9	27·5
10	2·980	0·980	10	35·1	24·7
12	2·900	0·918	12	31·5	22·2
15	2·635	0·835	14	28·4	20·0
20	2·260	0·716	16	25·7	18·0
25	1·985	0·641	18	23·4	16·4
30	1·769	0·572	20	21·3	14·9
40	1·414	0·459	22	19·4	13·5
50	1·204	0·393	30	13·8	9·5
60	1·006	0·329	40	9·4	6·3
70	0·848	0·279	50	6·5	4·1
80	0·672	0·223	60	4·9	2·9
90	0·380	0·127	70	3·8	1·9
100	0·000	0·000	80	3·0	1·2

L. W. Winkler represents the absorption coeff. of chlorine in water at $\theta°$ by the formula: $3·0361 - 0·46197\theta + 0·0001107\theta^2$. The solubility curve really represents the increasing solubility of chlorine hydrate, and the decreasing solubility of chlorine gas with rising temp. The maximum, about 9·6°, occurs when the latter begins to predominate over the former. The solubility of chlorine in water, and the solubility when the gas is mixed with hydrogen or carbon dioxide, is greater, between 13° and 38°, than corresponds with its partial press.[3] According to L. W. Winkler, however, bromine vapour dissolves in water in accord with Henry's law. The soln. of chlorine in water is called **chlorine water,** or *aqua chlorata*; and the soln. of bromine in water, **bromine water,** or *aqua bromata*. The solubility of liquid bromine in water, represented by the number of grams of bromine in 100 grms. of the soln., is

	0°	5°	10°	15°	20°	25	30°	40°	50°
Water . . .	4·17	3·92	3·74	3·65	3·58	3·48	3·44	3·45	3·52
Solubility . .	3·98	3·77	3·61	3·52	3·46	3·36	3·32	3·33	3·40

The solubility of iodine in water has not been so closely investigated as that of chlorine or bromine,[4] and the determinations are not in close agreement. H. Hartley and N. P. Campbell found that water dissolves

	0°	18°	25°	35°	45°	55°	60°	
Iodine .	0·1620	0·2765	0·3395	0·4661	0·6474	0·9222	0·9566	grms. per litre

The value at 0° is by G. Jones and M. L. Hartmann, and that at 60° by

R. Luther and G. V. Sammet. The soln. require one to two days to reach the point of sat. and they are brownish-yellow in colour.

Crystals of **chlorine hydrate** or of **bromine hydrate** are readily formed when aq. soln. of chlorine or bromine respectively are cooled to about 0°. According to J. Pelouze crystals of chlorine hydrate are formed when a few drops of hydrochloric acid are added to an aq. soln. of hypochlorous acid[5] cooled to about 2° or 3°. A. Ditte sealed chlorine hydrate, containing an excess of water, in a long bent Λ-tube. The leg containing the hydrate was warmed, and the chlorine was condensed to a liquid in the cold leg of the tube by the press. of its own vapour. When the apparatus was slowly cooled, fine fern-like crystals of the hydrate re-form on the surface of the water. On standing some time, these crystals disappear re-forming isolated greenish-yellow crystals about 2 or 3 mm. long. These crystals are highly refracting, and belong to the cubic system. The crystals of either hydrate are formed by leading the gas or vapour through a tube cooled to about 4° and moistened on the inside with water. In winter time, pipes[6] conveying chlorine gas may become clogged by the formation of the hydrate.

Chlorine hydrate was formerly thought to be solidified chlorine, but H. Davy demonstrated that the crystals contained water. The yellow crystals of chlorine hydrate examined by M. Faraday[7] (1832) contained 27·7 per cent. of chlorine and 72·3 per cent. of water; this is nearly eq. to $Cl.5H_2O$, or to $Cl_2.10H_2O$, and he added, "I have chosen it because it gave the largest proportion of chlorine of any experiment I made;" and owing to inevitable losses of chlorine in drying, he said, "It is even possible that this proportion of chlorine is under-rated, but I believe it to be near the truth." H. W. B. Roozeboom (1884) makes the proportion $Cl_2.8H_2O$, and R. de Forcrand (1901), $Cl_2.7H_2O$. The existence of the hydrates, $Cl_2.12H_2O$; $Cl_2.7H_2O$; and $Cl_2.4H_2O$, reported by G. Maumené, have not been confirmed. Hyacinth-red octahedral crystals of bromine hydrate, sp. gr. 1·49 (4°), were obtained by C. Löwig in 1829; their composition was determined by W. Alexejeff in 1876, and by H. W. B. Roozeboom (1884), whose analyses agree with the formula, $Br_2.10H_2O$. H. Giran's thermal analysis of the binary system $Br\text{-}H_2O$, and his analyses of the crystals, agree with the formula $Br_2.8H_2O$.

According to M. Faraday, the crystals of chlorine hydrate may be sublimed without decomposition in a sealed tube at 15·5° (M. Faraday), or at 20° (E. Biewend)[8]; but according to F. Wöhler at 38°, they form two liquids—one rich in chlorine, is a soln. of water in chlorine; and the other rich in water, is a soln. of chlorine in water; according to W. Alexejeff, bromine hydrate also decomposes into two analogous layers at 15°. In both cases the hydrate is re-formed on cooling to 0°. The critical temp. of decomposition of chlorine hydrate in open vessels is 9·6°, and in closed vessels, 28·7°. According to H. W. B. Roozeboom, the dissociation press. of chlorine hydrate from −10° to −0·24° is between 156 and 248 mm.; and between −0·24° and 28·7°, from 248 mm. to 6 atm. There are turning-points in the curve at −0·24° and 28·7°. F. Isambert's[9] measurements of the dissociation press. of chlorine hydrate between 0° and 14·5° agree fairly well with those of H. W. B. Roozeboom. According to the latter, the decomposition tension of bromine hydrate from −10° to −0·3° is from 25 to 43 mm.; from −0·3° to 6·2°, 43 to 93 mm. Above 6·2°, bromine hydrate crystals form an emulsion of water and bromine which slowly separates into two liquids—(i) a soln. of water in bromine and (ii) a soln. of bromine in water. In open vessels, under atm. press., bromine hydrate decomposes at 6·8°; at higher press. the decomposition temp. is still higher—at 150 atm. of oxygen press., it is stable at 20°, according to P. Villard;[10] and at 200 atm. of hydrogen press., it is stable at +9°. The increased stability of the hydrate in compressed oxygen is connected with the great solvent power of compressed oxygen gas for bromine vapour, and the consequent increased partial press. of the atm. of bromine on the hydrate.

P. Villard has measured the influence of compressed gases on the vapour press. of liquid bromine, and he found that bromine vapour is fairly soluble in compressed oxygen

such that at 300 atm. press. compressed oxygen takes up six times the normal amount: if the press. is released, the oxygen gives up the dissolved bromine in the form of small drops. The greater the press. the greater the amount of bromine dissolved by the compressure oxygen, and the deeper the colour. Compressed nitrous oxide takes up the same amount of bromine at 20 atm. press. as it does at 40 atm. Iodine also volatilizes in compressed oxygen and in compressed methane, and crystallizes out when the press. is relieved. Ethylene gas at 300 atm. press. is coloured deep violet by the dissolution of iodine, and the colour gradually disappears on standing owing to the union of the iodine with the ethylene. An interesting illustration of the dissolution of vapours by compressed gases is furnished by methane which dissolves its own volume of ethyl chloride, C_2H_5Cl, at 180 atm.; at 200 atm. press., the two substances are miscible in all proportions, and the surface of separation between liquid and gas disappears. P. Villard proposes to take advantage of the property for the distillation of substances decomposed by heat. The vapour is dissolved when the gas is compressed and rejected when the press. is relieved.

H. W. B. Roozeboom has measured the solubility of chlorine and bromine hydrates in water and expressed his results in terms of "grams of chlorine per 100 grms. of soln." He found that 100 grms. of soln. contain 0·492 grm. of chlorine at −0·24°, at which temp. the solid phase present is a mixture of ice and chlorine hydrate, $Cl_2.8H_2O$. Between 0° and 28·7° the solid phase is the hydrate alone, and the soln. has

	0°	2°	4°	6°	8°	9°	20°	28·7°	
Chlorine	0·533	0·644	0·732	0·823	0·917	0·937	1·85	3·69	per cent.

The binary system has not been completely explored. Similarly with bromine hydrate 100 grms. of soln. dissolve 2·17 grms of bromine at −0·30°, and the solid phase is ice and the hydrate $Br_2.10H_2O$. Between −0·3° and 6·2°, the solid phase is the hydrate, $Br_2.10H_2O$, alone, and the soln. has

	−0·2°	0°	3°	6°	6·2°	
Bromine . .	2·25	2·31	2·97	3·50	3·53	per cent.

In the latter case, there are two soln., one layer contains a soln. of bromine in water, the other, a soln. of water in bromine. There is an unstable system with ice as the solid phase at −3·7° with 3·03 grms. of *bromine*, *which may form before the hydrate*, $Br_2.10H_2O$, separates.

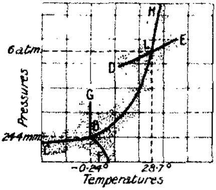

FIG. 20.—Equilibrium in the Binary System: Water-chlorine.

In the system Cl_2+H_2O, there are two components, just indicated; two solid phases—ice and chlorine hydrate, $Cl_2.8H_2O$; two soln.—one a soln. of water in an excess of chlorine, Sol. I, and a soln. of chlorine in an excess of water, Sol. II; and a gas phase—a mixture of chlorine and water vapour in varying proportions. The system has not been completely studied, but sufficient is known to show that the equilibrium curves take the form shown diagrammatically in Fig. 20. The two invariant systems L and B have four coexisting phases—L (28·7°; 6 atm.) denotes the point at which the hydrate decomposes—ice, Sol. I, Sol. II, vapour; B (−0·24°; 244 mm.) is a eutectic point—ice, hydrate, soln., vapour. The univariant systems with three coexisting phases comprise the curves: *BL*—hydrate, Sol. II, vapour; *DL*—hydrate, Sol. I, vapour; *LE*—Sol. I, Sol. II, vapour; *LH*—hydrate, Sol. I, Sol. II; *CB*—hydrate, ice, vapour; *BF*—ice, Sol. II, vapour; *BG*—ice, hydrate, Sol. II. The bivariant systems, representing two coexisting phases, are included in the areas bounded by the curves.

A similar result was obtained with the system Br_2+H_2O, where the hydrate is $Br_2.10H_2O$, and the invariant systems occur at the two quadruple points: L (6·2°; 93 mm.) and B (−0·3°; 43 mm.). Iodine forms no known hydrate with water.

W. L. Goodwin's values for the **specific gravity** of chlorine water—presumably sat. at the temp. indicated—are

Temp. . .	2·5	8·0	16·3	23	24	25·5°
Sp. gr. . .	1·00106	0·00494	1·00424	1·000264	1·00069	0·99984

The value for water at 2·5° was 0·99980; and at 25·5°, 0·994247. The specific gravity of bromine water was measured by J. Slessor [11] in 1858, and for soln. containing w grms. of bromine in 100 grms. of water, he found

w .	1·072	1·205	1·231	1·874–1·906	1·952–2·009	2·089–2·155	3·102–3·169
Sp. gr.	1·00901	1·00955	1·01223	1·01491	1·01585	1·01807	1·02367

The last-named soln. was sat.

According to T. J. Baker,[12] the **molecular heat of solution** of chlorine in water is 4·97 Cals., and according to J. Thomsen, 4·87 Cals. M. Berthelot places this constant between 3 and 7·5 Cals.—the indefiniteness is due to a reaction between chlorine and the water. H. le Chatelier estimates that a mol. of liquid bromine dissolving in water develops 1·08 Cals. From the effect of temp. on the absorption coeff., β, the heat of soln. Q of bromine vapour in water is $Q = -RT^2(d \log \beta/dT)$; or $Q = 1{\cdot}571T^2(d \log \beta/dT)$. For bromine vapour, Q, at 0° is 8·35 Cals., and at 60°, 6·5 Cals. If λ denotes the latent heat of vaporization, the heat of soln. of a mol. of liquid bromine in water will be $\lambda + Q$, where $\lambda = 7696 - 8{\cdot}48\theta$ Cals. The values of the heat of soln. of liquid bromine are very small, and become negative at about 40°. S. U. Pickering found a mol. of bromine absorbed 1·508 Cals. when dissolved in 2700 mols. of water. H. Hartley and N. P. Campbell estimated the heat of soln. of iodine to be 5·09 Cals. at 21·5° and 7·38 Cals. at 50°. G. N. Lewis and M. Randall calculate the free energy of formation of a mol. of an aq. soln. from the solid at 25° or 298° K., is 3926 cals., or $-RT \log 0{\cdot}0132$. The **diffusion coefficient** [13] of chlorine in aq. soln. containing 0·1 mol. per litre is 1·22 grms. per sq. cm. per day at 12°; 0·8 for bromine; and 0·9 for iodine. F. A. Henglein has made observations on the vap. press. of aq. soln. of chlorine, bromine, and iodine.

The **molecular conductivity** of aq. soln. of chlorine were found by A. A. Jakowkin [14] to be rather large. If v denotes the number of litres containing a mol. of chlorine, the molecular conductivity is, at 0°

v	17·18	43·33	99·01	195·0	372·7	551	2204
μ	79·63	129·5	183·0	221·1	241·4	244	247·5

and at 25°

v	11·74	22·96	45·12	91·84	306	732	2928
μ	138	200·2	270	338	392	396	396·5

At high dil., therefore, the conductivity is not far from that of hydrochloric acid. A. A. Jakowkin's explanation turns on the assumption, for which there is much confirmatory evidence, that in aq. soln., the chlorine is hydrolyzed forming hypochlorous acid, HOCl, and hydrochloric acid: $Cl_2 + H_2O \rightleftharpoons HCl + HOCl$, and the high conductivity, with highly dil. soln. shows that the hydrolysis is nearly complete. According to A. A. Jakowkin, about one-tenth of the chlorine in a sat. soln. at 0° is hydrolyzed.

The partition law.—If $a_1, b_1, c_1, \ldots$ denote the concentrations of a gas dissolved in a given liquid and $a_2, b_2, c_2, \ldots$ the corresponding concentrations of the gas in the space above the liquid, Henry's law means that

$$\frac{a_1}{a_2} = \frac{b_1}{b_2} = \frac{c_1}{c_2} = \ldots = \text{Constant}$$

This law, applicable for the distribution of a soluble gas between a liquid solvent and the space above, can be extended to include the distribution of a solute between

two immiscible solvents—*e.g.* iodine or bromine between water and ether, water and benzene, and between water and carbon disulphide; as well as silver or gold between molten lead and zinc; ferric chloride between ether and water, etc. This fact was indicated by M. Berthelot and E. Jungfleisch [15] in their paper: *Sur les lois qui président au partage d'un corps entre deux dissolvants.* In illustration iodine or bromine in a mixture of immiscible water and carbon disulphide divides itself so that the ratio of the concentrations of the solute in each layer is always the same. This constant is sometimes called the **partition coefficient.** Berthelot and Jungfleisch's results in Table IV illustrate the principle: the concentrations of the halogens

TABLE IV.—PARTITION COEFFICIENT OF IODINE AND BROMINE BETWEEN WATER AND CARBON DISULPHIDE.

Iodine.			Bromine.		
Water	CS_2	Quotient.	Water.	CS_2	Quotient.
0·0041	1·74	0·00238	0·0300	2·46	0·0122
0·0031	1·29	0·00250	0·0200	1·55	0·0128
0·0016	1·66	0·00244	0·0011	0·09	0·0125
0·0010	0·41	0·00244			

in the solvent indicated in the first two columns of each table refer to the amounts of solute in 10 c.c. of solvent. Although the constants are not uniformly the same, the deviations are within the range of experimental error. Later measurements, by A. A. Jakowkin and others, between water and carbon tetrachloride, bromoform, amyl-alcohol, or carbon disulphide made under better conditions, give smaller deviations. Similarly, when an aq. soln. of hydrogen peroxide is shaken with amyl alcohol, the peroxide divides itself between the two solvents so that the ratio of the concentration of alcohol phase to the conc. of aq. phase has always the same numerical value at a given temp. Expressing concentrations in milligram-molecules per litre, H. T. Calvert (1901) found at 25°:

Amyl alcohol phase .	13·4	28·0	41·9	65·0	94·5	130·2
Aq. phase . . .	94·0	193·5	296·7	460·0	670·0	912·5
Quotient . . .	7·0	6·9	7·1	7·1	7·1	7·0

The facts are generalized in the so-called **Berthelot and Jungfleisch's partition law:** *When two immiscible solvents are simultaneously in contact with a substance soluble in both, the solute distributes itself so that the ratio of the concentrations of the solute in each solvent is constant.* Otherwise expressed:

$$\frac{\text{Concentration of solute in solvent A}}{\text{Concentration of solute in solvent B}} = \text{Constant, say } k.$$

If the ratio be unity, the concentrations of the solute in each solvent will be the same; if the ratio be far removed from unity, a correspondingly large proportion of the solute will be found in the one solvent which can be utilized to extract the soln. from the other solvent. *E.g.* ether will remove ferric chloride from its aq. soln., and since many other chlorides are almost insoluble in ether, the process is utilized in analysis for the separation of iron from the other elements; the solubility of cobalt thiocyanate in ether is utilized for the separation of cobalt; perchromic acid is similarly separated from its aq. soln. by ether; molten zinc extracts silver and gold from molten lead; the extraction of organic compounds from aq. soln. by shaking out with ether or other solvent is much used in organic laboratories.

If w_0 grms. of iodine be dissolved in unit quantity of water, and this be shaken up with unit quantity of immiscible carbon disulphide, it follows that a quantity w_1 will remain

in the aq. layer and w_0-w_1 will pass to the carbon disulphide, so that $w_1=k(w_0-w_1)$, o $w_1=w_0k/(1+k)$ remains in the aq. layer, and w_0-w_1 passes into carbon disulphide. A second extraction with the same quantity of carbon disulphide gives $w_2=k(w_1-w_2)$, or substituting the previous value of w_1, $w_2=w_0k^2/(1+k)^2$; and generally, after the *n*th extraction

$$w_n=w_0\left(\frac{k}{1+k}\right)^n$$

remains in the aq. layer—the greater the number, n, of extractions, the smaller the quantity of substance remaining in the aq. layer. It can be shown in a similar way that with a given quantity of the extracting liquid, a better separation is obtained after many extractions with small quantities of the liquid than by few extractions with large quantities. The extraction can never be theoretically complete; the smaller the value of k the greater the efficiency of the process. Thus, with 10 grms. each of iodine and bromine in the aqueous layer the second extraction will leave $10(0{\cdot}00244\div1{\cdot}00224)^2$, or 0·00006 grm. of iodine, and $10(0{\cdot}0125\div1{\cdot}0125)^2$, or 0·0016 grm. of bromine. The same principles obtain in washing precipitates.

Suppose that the molecules of the solute ammonia remain normal, NH_3, in one solvent, say water; and that the molecules of the ammonia partially or completely polymerize in the other solvent, say chloroform, such that $2NH_3\rightleftharpoons N_2H_6$. Then, for equilibrium, $C_0=k_1C^2{}_1$, where C_1 represents the conc. of the molecules of ammonia, NH_3, in water; and C_0 represents the conc. of the molecules of ammonia, N_2H_6, in the chloroform. Again, if the molecules of ammonia are polymerized only in the chloroform, and not in the water, then, $C_0=K_1C_1{}^2$, or $C_1=\sqrt{K_1C_0}$. W. Herz and M. Lewy (1906) tested this hypothesis by finding how the formula so deduced fitted the facts. The fit was quite satisfactory; this was taken to prove that the ammonia molecule doubles on itself in this solvent. The partition law thus furnishes a method of measuring the relative mol. wt. of a solute in a given solvent. If the partition coeff. be not constant, it is inferred that the assumed molecular conc. is different from that which actually obtains.

The constitution of chlorine water.—As already indicated numbers ranging from $Cl_2.10H_2O$ to $Cl_2.7H_2O$ have been given for the composition of the hydrate. C. F. Schönbein,[16] shortly after the discovery of hypochlorous acid, suggested that the chlorine in chlorine hydrate is present as hypochlorous and hydrochloric acids: $HCl.HOCl.9H_2O$, although no experimental evidence was given in support of the hypothesis. H. E. Roscoe sought for oxy-chlorine acids in chlorine water by passing a stream of carbon dioxide through the liquid, but found no signs of these acids in the more volatile portion. C. Göpner assumed that the presence of hypochlorous and hydrochloric acids in chlorine hydrate was proved by the fact that mercuric chloride is formed on treating the hydrate with mercury—*Wölter's reaction*; but R. Schiff argued that if chlorine hydrate contained hypochlorous acid, it should be rapidly decomposed in diffused daylight; but, unlike hypochlorous acid, chlorine hydrate is comparatively stable under these conditions. The smell of dry chlorine hydrate with its 28 per cent. of chlorine, is not so marked as that of a 0·7 per cent. soln. of chlorine. This shows that the vapour tension of the chlorine in chlorine hydrate is very small. R. Schiff also argues that the pale colour of chlorine hydrate is against the formula $HCl.HOCl.9H_2O$ for chlorine hydrate. The work of A. A. Jakowkin shows that a fractional portion of the chlorine in an aq. soln. is hydrolyzed as suggested by C. F. Schönbein (1847) and by N. A. E. Millon (1849).

A. A. Jakowkin[17] employed the partition coeff. between chlorine water and carbon tetrachloride for estimating the concentration of free non-hydrolyzed chlorine in a soln. of that gas. If the hydrolysis be neglected, and the assumption be made that the whole of the chlorine in the aq. soln. be present as dissolved free chlorine, the partition coeff. of chlorine between water and carbon tetrachloride changes from 13·8 to 5·2. This is taken to mean that something is wrong with the assumption that the total chlorine is free in aq. soln. A. A. Jakowkin calculated the degree of hydrolysis: $Cl_2+H_2O=HCl+HOCl$, from the conductivity measurements of the aq. soln., deducted the amount of hydrolyzed chlorine from the total chlorine, and

the remainder, when assumed to represent the chlorine in equilibrium with that in the carbon tetrachloride layer, gave a satisfactory partition coeff.—mean 20·0—as illustrated in Table V, where the concentrations are expressed in milligram-molecules per litre.

TABLE V.—PARTITION COEFFICIENT OF CHLORINE BETWEEN WATER AND CARBON TETRACHLORIDE AT 0°.

Total chlorine.		Hydrolyzed chlorine in aqueous layer, x.	Chlorine as Cl_2 in aqueous layer—$C_1(1-x)$	Partition coefficient $k=\frac{C_2}{C_1(1-x)}$
Aqueous layer C_1	CCl_4—layer C_2			
58·21	803·3	0·3185	39·67	20·25
38·36	464·6	0·4012	22·97	20·22
23·08	222·5	0·5180	11·12	20·10
16·33	127·4	0·6092	6·382	19·97
10·10	52·93	0·7320	2·707	19·55

The partition coeff. rises from 20·0 at 0° to 30·5 at 28·6°, and to 35·2 at 57·5°. The hydrolysis attains a maximum at about 90°. Hydrochloric and hypochlorous acids are inappreciably soluble in the carbon tetrachloride; and the proof that the molecules of chlorine dissolved in the carbon tetrachloride are present as Cl_2 molecules turns on the fact that the partition coeff. of chlorine between chlorine gas and carbon tetrachloride is constant in accord with Henry's law. Thus, representing concentrations in milligram-molecules per litre:

Chlorine in air . .	0·1109	0·2666	0·5365	0·8800
Chlorine in CCl_4 .	8·908	22·46	44·14	75·09
Quotient . .	0·0124	0·0119	0·0122	0·0117

The mean value of the partition coeff. is therefore 0·012. Hence, the chlorine in soln. has the same molecular state as chlorine gas. These observations also show that the solubility of chlorine in water does not follow Henry's law if the total chlorine in soln. be considered, because only that portion of the chlorine which is not hydrolyzed is partitioned between the liquid and the space above. If allowance be made for this, the partition coeff. between chlorine water and air is $20\times0\cdot012=0\cdot24$. Chlorine gas at one atm. press. contains $\frac{1}{22\cdot4}$ mol. per litre; hence, if the partition coeff. be 0·24, a litre of chlorine water in equilibrium with chlorine gas at one atm. press. and at 0° will contain $\frac{1}{22\cdot4}\times\frac{1}{0\cdot24}=0\cdot186$ mol. per litre, or 1·32 grms. of free chlorine and 146 grms. of hydrolyzed chlorine per 100 c.c. The solubility of chlorine in water is 0·089 mol. per litre, and of this 0·025 mol. is hydrolyzed. At 25°, there will be 0·081 mol. of non-hydrolyzed chlorine per litre.

The presence of hypochlorous acid in the aq. soln. is shown by leading a current of mixed air and chlorine through a flask of water between 90° and 95°, and condensing the products in a cooled flask. Hypochlorous acid is volatilized and condensed. S. U. Pickering[18] also showed in 1880 that when an aq. soln. of chlorine is boiled in an open vessel, a dil. soln. of hydrochloric acid remains after the expulsion of the free chlorine, and A. Richardson (1903) has shown that when chlorine water is distilled, the hydrochloric acid is eq. to the hypochlorous acid in the distillate. The presence of chlorides, hypochlorous, hydrochloric, and other acids diminish the hydrolysis in virtue of the mass action law: $Cl_2+H_2O\rightleftharpoons HCl+HOCl$. In consequence, the apparent solubility of chlorine will be diminished, since less will be needed for establishing equilibrium: $Cl_2+H_2O\rightleftharpoons HCl+HOCl$—unless the result be obscured by a reaction between the acid and the chlorine such as must occur when the soln. contains over about a gram of HCl per 100 c.c. of hydrochloric acid.

The partition coeff. of bromine between water and carbon tetrachloride, is so

nearly constant that the results are not much affected by hydrolysis. The greatest deviations occur with the more conc. soln. of bromine (over 3 grms. per litre). The low solubility of iodine prevents highly conc. soln. being employed, and the partition coeff. between water and carbon tetrachloride is fairly constant. The concentrations in Table VI are in grams per litre of soln.

TABLE VI.—PARTITION COEFFICIENT OF IODINE AND BROMINE BETWEEN CARBON TETRACHLORIDE AND WATER.

Bromine.			Iodine.		
In water.	In CCl_4	Coefficient.	In water.	In CCl_4	Coefficient.
14·42	545·20	37·82	0·2913	25·61	87·91
3·216	94·84	29·48	0·1934	16·54	85·51
0·7711	21·53	27·92	0·1934	16·54	85·30
0·4476	12·09	27·02	0·0818	6·966	85·15
0·2478	6·69	27·00	0·0516	4·42	85·51

The electrical conductivity of bromine water measured by W. C. Bray [19] is also referred to hydrolysis: $Br_2+H_2O \rightleftharpoons HOBr+HBr$ and a negligibly small part to the ionization of bromine itself: $Br_2 \rightleftharpoons Br^{\cdot}+Br'$. He made the hydrolysis constant of bromine water $2·4\times10^{-8}$; A. A. Jakowkin, that of chlorine water $4·48\times10^{-4}$. According to the measurements of G. Jones and M. L. Hartmann, the hydrolysis constant for iodine in water at 0° approximates 9×10^{-15}; and according to W. C. Bray, $0·6\times10^{-12}$ at 25°. It will be remembered that the hydrolysis constant is represented by K in the equation: $K[Br_2]=[H^{\cdot}][Br'][HOBr]$, where the symbols in brackets represent the concentration of the substances concerned in the balanced reaction, $H_2O+Br_2=HOBr+H^{\cdot}+Br'$, and the concentration of the water in the system is so large that the proportion which is concerned in the reaction is negligibly small. The value of K for bromine at 25° is nearly the geometrical mean of the hydrolysis constant of chlorine and iodine:

	Chlorine.	Bromine.	Iodine.
Hydrolysis constant, K (25°) .	$4·48\times10^{-4}$	$2·4\times10^{-8}$	$0·6\times10^{-12}$

At 0° the hydrolysis constant of iodine is 9×10^{-15}. The hydrolysis in iodine water is assumed to be $I_2+H_2O \rightleftharpoons HI+HIO$. The specific electrical conductivity of iodine water rises very rapidly to about 4×10^{-6} and then slowly to about 20×10^{-6}; this last effect is supposed to be due to a secondary reaction involving: $3I_2+3H_2O=5HI+HIO_3$.

The photochemical decomposition of chlorine water, bromine water, and iodine water.—In 1785, C. L. Berthollet [20] noticed that chlorine water is gradually decomposed by exposure to light, forming aq. hydrochloric acid and oxygen. He said:

> I have filled a flask quite full with dephlogisticated muriatic acid (chlorine water) and connected the neck of the flask with a pneumatic apparatus by means of a tube; on exposure to light, I saw a large number of bubbles of gas collect on all sides of the liquid, and after some days, I found in the vessel, connected with the flask by means of the tube, a quantity of an elastic fluid which was the purest vital air (oxygen). As the vital air was developed from the acid in the flask, so did the liquid lose its yellow colour, and appear as clear as water. The liquid did not bleach blue vegetable colouring matter, but only turned it red, and retained very little of the smell of dephlogisticated muriatic acid: it effervesced with alkalies, and in a word, the dephlogisticated muriatic acid was nothing more than common muriatic acid. In another flask, similarly filled with the same fluid, and covered with black paper, the liquid suffered no change, and no vital air was developed.

The explanation, on H. Davy's chlorine theory, is embodied in the equation: $2H_2O+2Cl_2 \rightleftharpoons 4HCl+O_2$; and, in agreement with W. H. Wollaston's observation

that the chemically active or actinic rays are the most refrangible. H. Davy (1812) also noted that rays at the violet end of the spectrum are more active in promoting the decomposition of chlorine water than the other rays. N. T. de Saussure (1790) also found that the rate of decomposition depends on the intensity of the light. He said in his memoir: *Effets chimiques de la lumière sur une haute montagne comparés avec les plaines : ceux qu'on observe dans les plaines :*

> As soon as light impinges on dephlogisticated muriatic acid, it is decomposed. . . . Since the decomposition takes place gradually, and its velocity, within certain limitations, is proportional to the intensity of the light, I had a notion in 1787 of trying if the quantity of oxygen which is developed in this reaction cannot be utilize : as a kind of photometer to measure the action of light.

The observations have been confirmed by T. Torosiewicz (1836),[21] who noticed the decomposition proceeds more rapidly in white than yellow glass; by J. W. Draper (1845); W. C. Wittwer (1855), etc. According to J. W. Draper, warming the chlorine water facilitates the action of light, but does not itself provoke the reaction; and he states that "the decomposition of water once begun in the sunbeams goes on afterwards in the dark." for a bulb of chlorine water which has been exposed to sunshine was placed in the dark and the quantity of gas given off during the first six hrs. was

	1st	2nd	3rd	4th	5th	6th hr
Gas evolved .	0·0162	0·0159	0·0086	0·0060	0·0038	0·0031 cub. in.

and thenceforth for four days in diminishing quantities. He says the evolution of gas is not altogether due to the gradual escape of oxygen formed while the liquid was exposed to the sun, and held in a state of temporary soln., nor to the decomposition of hydrogen peroxide or chlorous acid formed in the liquid. The quantity given off in the dark depends on the intensity of the light to which it was originally exposed, and on the time of exposure. The cause of the decomposition of insolated chlorine water in darkness was attributed to a change in the nature of the chlorine induced by exposure to the sun's rays. He says:

> Chlorine is *one of those allotropic bodies with a double form of existence—active and passive.* As commonly prepared it is in its passive state; but on exposure to the indigo *rays, or other causes, it changes and assumes an active form. In this latter state, its* affinity for hydrogen becomes so great that it decomposes water without difficulty.

The decomposition of chlorine water when placed in the sunbeam, adds J. W. Draper, does not begin at once, but a certain space of time intervenes, during which the chlorine is undergoing its specific change. R. Bunsen and H. E. Roscoe[22] do not consider that the modification which chlorine undergoes by exposure to light is so persistent as J. W. Draper records; possibly, said the latter, because "the insolation to which the chlorine was submitted was not continued sufficiently long, or perhaps the light was not sufficiently intense." There is no doubt that chlorine prepared under ordinary conditions can assume an active and a passive state, *vide infra.*

F. Wöhler[23] found that when chlorine hydrate in a sealed glass tube is exposed to sunlight, it forms two liquids, but does not decompose, since, after a summer's exposure, the two liquids re-form chlorine hydrate when winter returns. The same phenomena occur if the chlorine hydrate is warmed and cooled under similar conditions. A conc. soln. of chlorine water is far less prone to decomposition on exposure to sunlight than is a more dil. soln. J. M. Eder found the same to be the case with bromine water, but he also found that a conc. soln. of chlorine water lost 53·95 per cent. of chlorine while a dil. soln. lost 41·87 per cent. under similar conditions, but he does not state the concentration very exactly. A. Pedler further showed that soln. more conc. than one mols. of chlorine with 64 mol. of water had not decomposed perceptibly after a two months' exposure to tropical sunlight, and with that increasing dilution, the action became progressively greater, as illustrated in Table VII.

E. Klimenko[24] has confirmed the observation that dil. soln. of chlorine wat decompose more rapidly than conc. soln.: and he has studied the influence of hydr chloric acid and various chlorides on the action of sunlight on chlorine confined i sealed glass tubes. J. Billitzer found that the presence of small quantities o

TABLE VII.—ACTION OF TROPICAL SUNLIGHT ON CHLORINE WATER.

Mol. of water per mol. chlorine.	Time of exposure to actual sunlight.	Percentage of chlorine which had acted on the water.
64	2 mths.	nil
88	132 hrs.	29
130	137·1 ,,	46
140	137·1 ,,	29
412	137·1 ,,	78

hydrogen chloride increased the speed of decomposition but with larger amounts; E. Klimenko observed the speed of the reaction to be retarded by the presence of hydrochloric acid and chlorides, and this the more with the chlorides of the alkalies than with the chlorides of the alkaline earths; and the retardation is also greater with the elements of a given group the greater the at. wt. of the metal. For example, with soln. containing a mol. of the given salt per litre, and the same quantity of chlorine, the amount of chlorine remaining after the same exposure when referred to a tube with hydrochloric acid as unity, was as follows—HCl unity:

LiCl	NaCl	KCl	$CaCl_2$	$SrCl_2$	$BaCl_2$	$MgCl_2$	$ZnCl_2$	$CdCl_2$
0·3079	0·1732	0·0900	0·3901	0·3022	0·2846	0·530	0·2004	0·042

The quantity of chlorine which does not take part in the decomposition is independent of the time of exposure.

If a beam of light of intensity I_0 is changed by an amount $-dI$ in passing through a layer of fluid of thickness dx, it is assumed that $-dI$ is proportional to dx, and to I_0, so that $-dI=aI_0dx$, where a is a constant. By integration, the intensity I of the light after it has passed a layer of fluid of thickness x, is $I=I_0e^{-x}$. The constant a depends on the nature of the substance and the wave-length of the incident beam of light. It is called the **coefficient of absorption** of the substance for the light in question. If a beam of light traverses a thin layer of chlorine water of concentration C_0, W. C. Wittwer, in his paper *Ueber die Einwirkung des Lichte auf Chlorwasser* (1855), showed that the amount of hydrogen chloride, dC, formed in the time dt, is proportional to the concentration s of the chlorine water, and to the intensity I_0 of the incident light; or $dC=CIdt$, that is, the concentration C of the chlorine at the end of the time t is $C=C_0e^{-It}$. If the time is constant, and the layer of liquid have a thickness dS, the light changes $dI=-IC_0dS$, or the intensity of the light after it has traversed a layer S is $I=I_0e^{-aC_0S}$; and $I_0(1-e^{-aC_0S})$ represents the loss which the light has suffered in passing a distance dS. Hence, the change dC in the conc. of the chlorine water, initially C_0, when light of intensity I_0 traverses a layer of thickness S in the time dT will be $dC=CI_2(1-e^{-aC_0S})dt$, an expression which W. C. Wittwer found to be applicable to this reaction. By keeping the experimental conditions constant, this equation reduces to $dC=kCdt$, where k is a constant; if a denotes the initial concentration of the chlorine, and Sdx the amount decomposed in the time dt, $dx=k(a-x)dt$, and W. C. Wittwer's equation assumes the integrated form

$$k=\frac{I}{t}\log\frac{a}{a-x}$$

This equation is valid for pure chlorine water when the conditions are such that the field may be regarded as uniform; the constant k, however, increases as the

chlorine is consumed because the field of illumination becomes more uniform the more dil. the soln. If chlorides are present in the soln., H. Tuchel assumed that part of the chlorine in soln. is present as trichloride, and this portion of the gas is not directly concerned in the reaction: $2H_2O+2Cl_2=4HCl+O_2$. If ξ denotes the initial concentration of the chlorine directly concerned in this reaction, the preceding equation reduces to the form:

$$k=\frac{1}{t}\log\frac{\xi}{\xi-x}$$

which is applicable to the decomposition of soln. of chlorides in water, when $a-\xi$ represents the amount of chlorine which does not take a direct part in the decomposition, $2H_2O+2Cl_2=4HCl+O_2$. Only for pure chlorine water does $a=\xi$.

According to C. F. Bärwald and A. Monheim (1835), the decomposition is accelerated by the presence of organic substances. J. Milbauer tried the effect of thirty-two metal chlorides: of sodium tungstate and molybdate; of uranyl sulphate; and of sulphuric, selenic, arsenic, and boric acids on the photo-decomposition of chlorine water, and found that none accelerated but that most retarded the action. Chlorine catalyzes the decomposition of bromine water; and bromine, chlorine water; while iodine does not accelerate, but rather retards the reaction, probably by forming relatively stable iodine compounds. A. Benrath and H. Tuchel found the temp. coeff. of the velocity of the reaction with chlorine water between 5° and 30° increases in the ratio 1 : 1·395 per 10°.

The hydrolytic reaction between water and chlorine results in the formation of hypochlorous acid: $H_2O+Cl_2=HCl+HOCl$; and in feeble diffused daylight, the hypochlorous acid is decomposed into chloric acid and oxygen: $3HOCl=2HCl+HClO_3$, according to E. Klimenko; or $8HClO=2HClO_3+6HCl+O_2$, according to A. Pedler,[25] so that chloric acid is always found among the products of the decomposition. Aq. soln. of chloric acid alone are not decomposed by light; but this does not apply with chloric acid in the presence of hydrochloric acid. G. Gore found the electromotive force of chlorine water decomposing in light gradually diminishes to a minimum value when the soln. contains hydrochloric, chloric, and hypochlorous acids; on further exposure, the electromotive force increases slowly until the soln. contains nothing but hydrochloric acid and hydtogen peroxide. Hence, says G. Gore, these are two essentially different phases in the reaction—(i) the formation of chlorine acids; (ii) the decomposition of these acids into hydrochloric acid and hydrogen peroxide, but the presence of the last-named compound has not been confirmed. A. Popper could detect no perchloric acid in the products of the reaction; but J. Billitzer has reported the presence of traces of this acid. According to A. Pedier, the more conc. the soln. of chlorine water, the more nearly do the products formed by the action of light approach the values indicated in the equation: $2H_2O+2Cl_2=4HCl+O_2$, but as the amount of water is increased, the proportion of chloric acid in the product increases. The side reactions which occur in the decomposition of insolated chlorine water, and the effect of the various products of decomposition on the speed of the change, render the reaction, $2H_2O+2Cl_2=4HCl+O_2$, an unreliable foundation for the construction of such a photometer as was suggested by N. T. de Saussure (1790) to measure the intensity of light in terms of the volume of oxygen evolved; similar remarks apply to W. C. Wittwer's[26] photometer which was based on the decomposition of a 0·1 to 0·4 per cent. soln. of chlorine water. R. Bunsen and H. E. Roscoe also said that the many sources of error involved in the measurement of the intensity of light by the chlorine water photometer make the results of no value.

According to C. Löwig,[27] bromine water in light behaves in a similar way to that of chlorine water, but as J. M. Eder showed, bromine water is much less sensitive to light in that it decomposes with but one-sixth or one-twelfth the speed of chlorine

water. The presence of tartaric or citric acid accelerates the decomposition of chlorine or bromine water in light. According to C. F. Cross and A. Higgin, water is not decomposed by bromine or iodine if heated eight days in a sealed tube at 160°, but if a metal salt be present like lead acetate, the bromide or iodide is precipitated. H. W. Vogel states that iodine water is stable in light. According to H. Bordier, **X-rays,** like light, decolorize dil. aq. soln. of iodine or starch iodide; and the X-rays effect a change in a few minutes which requires several hours with ultra-violet light.

The solubility of the halogens in acid and salt solutions.—The solubility of chlorine in various salt soln. has been determined by W. L. Goodwin,[28] E. G. Kumpf, C. A. Kohn and F. O'Brien, etc. W. L. Goodwin used the chlorides of lithium, sodium, potassium, calcium, strontium, barium, magnesium, cadmium, iron(ic), cobalt, nickel, and manganese, and found the solubility is increased by the presence of hydrogen chloride, but is in general decreased by the presence of the other chlorides. The decrease is very marked with the conc. soln. of sodium chloride. The solubility of chlorine in sulphuryl chloride, SO_2Cl_2, has been studied by H. Schulze; in chromyl chloride, CrO_2Cl_2, by H. W. B. Roozeboom; in soln. of sodium chloride, by E. O. Mandala; and in arsenious chloride, $AsCl_3$, by B. E. Sloan. Some results at atm. press. are indicated in Table VIII.

TABLE VIII.—SOLUBILITY OF CHLORINE IN SALTS SOLUTIONS.

Temperature.	Solubility coefficients						
	Water.	Hydrochloric acid.		In 20 per cent. KCl.	In 11·41 per cent. LiCl.	Sodium chloride per cent.	
		Sp. gr. 1·046.	Sp. gr. 1·125.			9·97	26·39
0°	—	4·1	7·3	1·5	2·8	2·3	0·50
5°	2·0	5·1	6·7	2·0	2·4	2·0	0·44
10°	2·7	4·1	6·1	2·2	2·4	1·7	0·40
15°	2·6	3·5	5 5	1·6	2·0	1·4	0·36
20°	2·3	3·0	4·7	1·2	1·6	1·2	0·34
25°	2·06	2·5	4·0	1·0	1·4	0·94	0·30
30°	1·8	2·0	—	0·9	1·3	—	—
40°	1·35	1·25	—	—	—	—	—
50°	1·0	—	—	—	—	—	0·2
80°	—	—	—	—	—	—	0·05

W. L. Goodwin carried the solubility curves down to temp. at which chlorine ıydrate was formed, and he noticed (1) that the solubility curve increased with ising temp. to about 10°, as in the case of chlorine in water; and (2) that the presence f chlorides in soln. lowers the temp. at which the maximum appears, and also the emp. at which the hydrate separates. Otherwise expressed, the presence of hlorides in soln. hinders the formation of chlorine hydrate. The increased solu-ility of chlorine with an increase in the conc. of the hydrochloric acid may be noted. I. E. Roscoe[29] found that the coeff. of absorption of chlorine was *lowered* from 2·39 o 1·98 at 14° by $\frac{1}{120}$th part of hydrochloric acid. M. Berthelot found that the bsorption coeff. was *raised* in presence of hydrochloric acid, for a 38 per cent. oln. of hydrogen chloride absorbs 17·3 grms. of chlorine per litre; a 33 per cent. oln. 11 grms.; and a 3 per cent. soln. 6 grms. of chlorine per litre. At 21° the solu-ility of chlorine in a dil. hydrochloric acid decreases with increasing conc. of the id, to 1·50 with a 0·94 per cent. of soln. of HCl. This corresponds with the general haviour of chlorine in aq. soln. of the other chlorides. After this, the solubility rve of chlorine almost doubles on itself, for the solubility of the chlorine now creases with increasing conc. of acid up to a solubility of 38·2 with a 31·2 per cent. ln. of HCl. The increase was attributed by J. W. Draper (1843) to the possible

formation of a bichloride of hydrogen, and by M. Berthelot (1881) to the formation of hydrogen perchloride, HCl_3. This was confirmed by the fact that the heat of soln. of a mol. of chlorine in hydrochloric acid is much greater than in pure water—with water, the heat of soln. is 7·5 Cals., and with $HCl+4·5H_2O$, 9·4 Cals. M. Berthelot's hypothesis is the most probable explanation of the phenomenon, although there is nothing in the experimental data to show that particular polychloride is formed. This hypothesis is also in line with the behaviour of the other halogens in soln. of the corresponding alkali halide, or haloid acid.

The general effect of the presence of a salt in soln. is to reduce the solubility of bromine,[30] and this the more the greater the conc. of the salt. For example, with a $\frac{1}{10}N$-soln. of sodium nitrate, 3·374 grms. of bromine were dissolved per 100 c.c., and with a N-soln., 2·88 grms., while the solubility of bromine in water at 25° is 3·395 grms. per 100 c.c. The effect of a few typical salts, in grms. per 100 c.c., on the solubility of bromine—grams per 100 c.c.—in water is as follows:

	K_2SO_4	$NaNO_3$	$NaCl$	$(NH_4)_2SO_4$	$CH_3.COONH_4$	H_2SO_4
Salt . .	9·118	8·509	5·850	7·004	7·709	4·903
Bromine .	2·48	2·80	5·590	7·77	34·05	2·936

The increase in the solubility of bromine in soln. of ammonium salts is very marked, as is also the case with the alkali chlorides. The case with the alkali bromides is specially interesting. The solubilities by F. P. Worley are indicated in Table IX. The marked increase in the solubility of bromine in soln. of potassium bromide was attributed by M. Roloff to the formation of molecules of KBr_3. He shook up a soln. of bromine in carbon disulphide with water and with an aq. soln. of potassium bromide, and measured the concentration of the bromine in the two layers. M. Wildermann has shown that the density of bromine vapour over a soln. of potassium bromide sat. with bromine is the same as over water sat. with bromine, indicating that the conc. of the free bromine in all the aq. soln. is the same, and any excess in the presence of potassium bromide must be united with the potassium bromide. All the bromine dissolved by a soln. of potassium bromide can be removed

TABLE IX.—SOLUBILITY OF BROMINE IN SOLUTIONS OF POTASSIUM BROMIDE (F. P. WORLEY).

Potassium bromide per litre of solution.		Bromine dissolved per litre.			
		26·5°		18·5	
Mol.	Grms.	Gram-atoms.	Grms.	Gram-atoms.	Grms.
0	0	0 43	34·23	0·445	25·56
0·02	2·18	0·47	37·35	0·48	38·56
0·04	4·38	0·57	40·79	0·52	41·91
0·06	6·55	0·55	44·21	0·57	45·31
0·08	8·76	0·59	47·33	0·61	48·44
0·10	10·91	0·65	51·87	0·65	52·23
0·20	21·82	0·86	68·67	0·87	69·69
0·40	43·82	1·27	101·60	1·31	104·90
0·60	65·46	1·67	133·70	1·77	141·60
0·80	87·64	2·10	168·10	2·23	178·70
0·90	98·19	2·335	186·20	2·485	198·70

by successive extractions with carbon disulphide, or by a stream of air. Hence it must be assumed that the polybromide formed is stable only in the presence of free bromine. For equilibrium, $KBr_{n+1} \rightleftharpoons KBr + \frac{1}{2}nBr_2$, and that there is a progressive dissociation of the polybromide, KBr_{n+1} as the conc. of the free bromine is diminished. Table IX shows that if the amount of bromine dissolved by the water

be assumed constant, and the result be subtracted from that actually dissolved, th increase in the solubility of bromine is directly proportional to the amount o potassium bromide in the more dil. soln. Hence it is probable the whole of th potassium bromide in soln. unites with bromine to form the polybromide. Th effect of a variation of temp. is negligibly small, and consequently it is inferred tha the polybromide is not appreciably dissociated at these temp., since it is not likely that if the polybromide is partly dissociated, the degree of dissociation will be independent of temp. With these assumptions, the amount of bromine dissolved by the more dil. soln. of potassium bromide corresponds with the amount required to convert all the dissolved potassium bromide, KBr, into potassium tribromide, KBr_3. The still greater solubility of bromine in soln. containing over 0·1 mol. of potassium bromide per litre is taken to indicate a tendency to the formation of a still more complex polybromide, say, the pentabromide, KBr_5—*vide* § 11 in the next chapter.

J. M. Bell and M. L. Buckley found the solubilities of bromine (*n* gram-atoms per litre) in soln. of sodium bromide containing *w* grms. per litre, at 25°:

w . . .	92·6	160·5	205·8	255·8	319·7	359·0	408·3
n . . .	2·479	4·345	6·195	8·575	13·65	16·04	20·85
Sp. gr. . .	1·213	1·372	1·515	1·678	1·997	2·137	2·420

A. F. Joseph gave for the solubility of bromine in aq. soln. of potassium bromide or rather the converse, in grams per 100 grms. of water at 32·4°:

w .	725·6	733·9	740·7	750·2	764·3	771·1	801·3	845·9
n .	0	24·0	39·6	74·3	120·9	137·2	229·7	382·1
Sp. gr.	1·3917	1·4063	1·4132	1·4356	1·4633	1·4753	1·5236	1·5980

A. F. Joseph found that the solubility of potassium bromide in water is increased by the addition of bromine. For moderate conc., about half a mol. of bromide is dissolved for each mol. of bromine added to the water. This corresponds with that required for the formation of potassium tribromide. The limit of the solvent capacity of water was not reached with soln. containing over 2000 grms. per litre. There is, however, a maximum vol. conc. of bromide which corresponds with between 200 and 2000 grms. of bromine per litre.

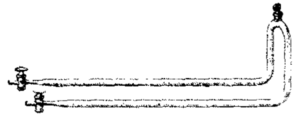

FIG. 21.—F. P. Worley's Apparatus.

By assuming a definite formula for the polybromide attempts have been made to show that the relative proportions of the substance concerned in the reaction are in accord with the law of mass action. For example, with the polybromide $KBr.nBr_2$ of conc. C, where the dissociation products are KBr of conc. c_1, and nBr of conc. c_2, the equilibrium condition is that $KC=c_1c_2^n$, where K is the equilibrium constant. If the soln. are sat. with bromine, and the conc. of the free bromine in the soln. is constant, $K'C_1=c_1$, meaning that the conc. of the polybromide is proportional to the uncombined potassium bromide, and the constancy of the equilibrium constant is independent of the value of n. If the soln. are not sat. with bromine, the equation $KC=c_1c_2^n$ can be applied when the relative amounts of free bromine and of bromine combined as polybromide have been determined. No analytical process involving the removal of bromine from the system is applicable since the polybromide is decomposed as fast as the free bromide is removed. F. P. Worley obtained the desired data by simultaneously shaking, without mixing, two soln. of bromine—one in pure water, one in a soln. of potassium bromide of known conc. in an apparatus, Fig. 21, with a common vapour space for the two soln. When the system is in equilibrium, it is assumed that the conc. of the free bromine in the two soln. is the same, since each is in equilibrium with the same vapour space. The determination of the free bromine in the water is made by direct titration.

The results agree better with the assumption that $n=1$ than $n=2$, although in neither case is the value of K constant. This is taken to mean that a small amount of a polybromide, more complex than KBr_3, is also formed.

G. Jones and M. L. Hartmann's measurements of the electrical conductivity of aq. soln. of bromine in water and soln. of potassium bromide are interpreted to mean that bromine dissolves as Br_2; that this is followed by a reaction $Br_2+H_2O \rightleftharpoons HBrO+H^{\cdot}+Br'$; and simultaneously by $KBr+Br_2 \rightleftharpoons KBr_3$; and by $2Br_2+KBr \rightleftharpoons KBr_5$. A sat. soln. of bromine in water at 0° has the composition in mols. per litre: 0·2539 Br_2; 0·001085 $H^{\cdot}$; 0·000126 Br'; 0·00628 Br_3'; and 0·00331 Br_5'. The equilibrium constant K in $K_3[Br_3']=[Br'][Br_2]$ is 0·051; and in $K_5[Br_5']=[Br'][Br_2]^2$. The hydrolysis constant K' in $K[Br_2]=[H^{\cdot}][Br'][HOBr]$ is $5·7\times10^{-10}$. E. O. Mandala measured the solubility of bromine in hydrochloric and hydrobromic acids

The solubility of iodine in aq. soln. of various salts[31] is somewhat similar to the behaviour of these salts on the solubility of bromine. The solubility is reduced by sodium and potassium sulphates and nitrates; it is raised a little by potassium and sodium chlorides, and considerably by potassium and sodium bromides, ammonium salts also increase the solubility of iodine; boric acid has but little influence. C. Kraus found the solubility of iodine is considerably augmented in the presence of hydrochloric acid; phosphoric acid dissolves iodine slowly in the cold and rapidly when heated, and similarly also in acetic, tartaric, citric, and tannic acids. The solubility of iodine in conc. sulphuric acid (over 83 per cent.) is about 6·6 grms. per litre; *the colour is violet, which becomes yellow on dilution until, with 42 per cent.* acid, the colour is brown. According to W. Vaubel the absorption spectrum of the dil. soln. shows red, yellow, and green, but not blue absorption bands; with the yellow soln. there is no green band. A. Hantzsch and A. Vagt explain this by assuming a brown hydrate of iodine is formed if sufficient water be present, and when the conc. of the acid is great enough no brown hydrate is formed and the anhydrous iodine shows its characteristic violet colour. Soln. in nitric acid behave similarly. The solubility of iodine in potassium iodide soln. follows the same general character as that of bromine in soln. of potassium bromide, but the effects produced are more marked. This is illustrated in Table X.

TABLE X.—EFFECT OF POTASSIUM IODIDE ON THE SOLUBILITY OF IODINE.

Potassium iodide—per litre.		Iodine—per litre.	
Milligram-molecules.	Grams.	Milligram molecules, I_2	Grams.
0	0	1·342	0·340
0·830	1·37	1·814	0·461
1·661	2·75	2·235	0·568
3·322	5·51	3·052	0·775
6·643	11·03	4·667	1·185
13·29	22·07	8·003	2·032
26·57	44·15	14·680	3·728
53·15	88·30	28·030	7·119
106·30	176·60	55·280	14·040

A soln. of "twenty-two grains of iodine and thirty-three grains of iodide of potassium, in one ounce of distilled water" forms the *liquor iodi* of the British Pharmacopœia. The effects produced by the ammonium salts are attributed to their hydrolysis into ammonium hydroxide, and the consequent formation of ammonium iodide or polyiodide. The effects produced by soln. of the halide salts are doubtless due to the formation of polyiodides as in the analogous case with bromine and potassium bromide. A. A. Jakowkin allowed carbon disulphide to remain in contact with aq. soln. of iodine and potassium iodide until equilibrium was attained; and

assumed that any free iodine always divides itself between the water and carbon disulphide in the ratio 1 : 410, as is the case if potassium iodide be absent. Assume that in the aq. soln. there is the balanced system: $KI_3 \rightleftharpoons KI + I_2$. If x mol. of free iodine be contained in unit volume of the potassium iodide soln. which contains a mol. of potassium iodide, there will be present $1-x$ mol. of the complex KI_3, and $a-(1-x)$ mol. of potassium iodide. Consequently, by the law of mass-action $(1-x)K=(a-1+x)x$. A. A. Jakowkin was able to calculate the equilibrium constant K, and found the results in harmony with this assumption, for K varied between 1577×10^{-6} and 1808×10^{-6}; whereas with the assumption that the system is $KI_5 = KI + 2I_2$, K varied from $10{,}180\times10^{-6}$ to 461×10^{-6}. The argument does not apply to conc. soln. of potassium iodide, where there are indications of higher polyhalides than KI_3. With iodine and potassium bromide, mixed polyhalides are formed—*e.g.* potassium iodobromide, $KBrI_2$. The effect of chlorine on the alkali chlorides is thus quite different from the effects of the other two halogens on their alkali salts; and less than the effect of the other two potassium halides on the solubility of iodine. The solubility of iodine in *water* is 0·340 grm. per litre at 25°—E. O. Mandala and A. Angenica give 0·0334 per cent., or 0·00131 mol. per litre at 25°; with a normal soln. of *potassium chloride*, the solubility is 0·658; with a normal soln. of *potassium bromide*, 3·801; and with a normal soln. of *potassium iodide*, about 14 grms. per litre. E. O. Mandala and A. Angenica measured the solubilities of iodine in aq. soln. of various concentrations of *hydrochloric acid*, *hydrobromic acid*, and *hydriodic acid*, and found it to be equal to that in the soln. of the corresponding potassium salt of the same conc. Hence, the solubility of the iodine is specific to the halogen ion, and is independent of the nature of the positive ion of the halide. The f.p. of soln. of hydriodic and hydrobromic acids are not altered by the dissolution of iodine.

Iodine and bromine are fairly soluble in *arsenic chloride*, $AsCl_3$; [32] 100 grms. of this compound dissolve 8·42 grms. of iodine at 0°, 11·88 grms. at 15°, and 36·89 grms. at 96°. A little iodine and bromine dissolve in *sulphuryl chloride*, and the soln. conduct electricity. P. Walden explains the conductivity of, say, iodine by assuming the molecule of iodine is ionized into a positively and negatively charged iodine atom: $I_2 = I^{\cdot} + I'$. Iodine and bromine also form conducting soln. in liquid *sulphur dioxide*, and the soln. of iodine is violet; according to J. Inglis, the soln. of iodine in *sulphur chloride*, S_2Cl_2, is a conductor of electricity, and according to E. Solly, a non-conductor. Iodine dissolves in liquid *ammonia* forming, according to E. C. Franklin and C. A. Kraus, a series of substitution derivatives, NH_4I and $NI_3.nNH_3$, where n stands for 1, 2, or 3. The colour changes according to C. Hugot from black to red, to pale yellow. According to U. Antony and G. Magri liquid hydrogen sulphide forms a dark red soln. without perceptible reaction. F. Sestini found iodine soluble in liquid *sulphur trioxide* to the extent of about 200 grms. per litre; and E. H. Büchner that iodine dissolves in liquid *carbon dioxide* to the extent of 5 per cent., while bromine is slightly soluble in the same menstruum. According to B. D. Steele, D. McIntosh, and E. H. Archibald, bromine dissolves in liquid *hydrogen chloride* and raises its electrical conductivity.

The solubility of the halogens in organic solvents.—L. Bruner [33] has measured the solubility of iodine in mixtures of *ethyl alcohol* and water at 15°:

Alcohol .	10	20	40	60	80	90	100	per cent.
Iodine .	0·05	0·06	0·26	1·14	4·20	7·47	15·67	„ „

N. Schoorl and A. Regenborn say that owing to the ready formation of hydrogen iodide, accurate determinations of the solubility in aq. alcohol can be made only by making a sat. soln. of iodine in absolute alcohol, diluting the soln., and determining the iodine at once. The solubility follows a fairly regular course:

Per cent. alcohol .	100	95	90	80	60	40	20	10	0
Per cent. iodine .	20	14·8	11·4	7·2	2·3	0·55	0·08	0·045	0·025

When the amount of ethyl alcohol exceeds 18 per cent., the addition of water causes a precipitation of iodine, at lower alcohol conc. there is no precipitation. The maximum precipitation occurs when just enough water is added to bring the alcohol conc. to 18 per cent.

The *tinctura iodi* of the British Pharmacopœia is a soln. of "half an ounce of iodine, and a quarter of an ounce of potassium iodide in a pint of rectified spirit." P. Wäntig found the mol. ht. of soln. —1·941 Cals., and S. U. Pickering —1·714 per 880 mol. of ethyl alcohol. C. Löwig found that alcoholic tincture of bromine is slowly decomposed in darkness, rapidly in light. Alcoholic soln. of iodine, according to H. E. Barnard, are stable in light and in darkness, but according to J. M. Eder they decompose 1000 times more slowly than chlorine water under similar conditions; T. Budde has shown that hydriodic acid, acetic ester, and aldehyde are formed, and the electrical conductivity of the soln. increases. J. H. Mathews and E. H. Archibald and W. A. Patrick found a freshly prepared *N*-soln. to have an electrical conductivity of $2·4 \times 10^{-6}$ reciprocal ohms; and a sat. soln., $1·61 \times 10^{-4}$ reciprocal ohms at 25°. The decomposition is accelerated by the presence of platinum. The heat of soln. decreases with concentration from —7·92 to —7·42 cals. respectively for dilute and sat. soln. in methyl alcohol, and likewise from —4·88 to —5·22 cals. for similar soln. in ethyl alcohol. The solubility of iodine in aq. soln. of *propyl alcohol* is not very different from that in ethyl alcohol.

H. Arctowsky has measured the solubility of iodine in benzene, chloroform, ether, and carbon disulphide—in some cases at very low temp. At —83°, 100 grms. of a sat. soln. of iodine in *ether* contain 15·39 grms. of iodine, and at —108°, 15·09 grms. S. U. Pickering found the mol. ht. of soln. —1·536 per 800 mol. of ether. The following results are expressed in grams of iodine dissolved per 100 grms. of the soln. P. Walden has measured the electrical conductivity of ethereal soln. of iodine; the conductivity increases with time, probably owing to chemical changes. According to J. Traube, iodine reacts with both ether and alcohol if heated in sealed tubes; and according to D. McIntosh with ether, forming $C_4H_{10}O.Cl_2$ at —51°. The solubility of iodine in *benzene* is :

	4·7°	6·6°	10·5°	13·7°	16·8°
Iodine . .	8·08	8·63	9·60	10·44	11·23 per cent.

and the mol. ht. of soln. is —4·681 Cals. according to P. Wäntig, or —6·114 Cals. per 1200 mol. of benzene according to S. U. Pickering. The viscosity of a soln. of bromine in benzene is 0·00737 at 12°. The diffusion constant of iodine in benzene is 1·41 grm. and of bromine in benzene 1·75 per sq. cm. per day. L. Bruner noticed that soln. of iodine in *nitrobenzene* conduct electricity, but not if all is thoroughly dried with phosphorus pentoxide. H. M. Dawson found that 100 c.c. of nitrobenzene dissolved 5·077 grms. of iodine. A. F. Joseph measured the solubility of potassium bromide in soln. of bromine in nitrobenzene.

In *chloroform* under similar conditions: at —73·5°, the solubility of iodine is 0·080; at —60°, 0·129; at —49°, 0·188; and, according to W. Duncan, at 10°, 1·77, or one part of iodine required 5·66 parts of chloroform for soln. According to E. Beckmann and P. Wäntig, in the proximity of the f.p. of chloroform, —61°, almost all the iodine separates from the soln. and only 0·0164 per cent. remains. A. Hantzsch and A. Vagt give for the solubility in chloroform at 0°, 1·96; at 18°, 3·78; and at 30°, 5·56 grms. of iodine per 100 grms. of soln. The mol. ht. of soln. is —5·484 Cals. according to E. Wäntig, or —6·014 Cals., according to S. U. Pickering, per 740 mol. of chloroform. A. A. Jakowkin gives for *bromoform* at 25°, 18·955 grms. of iodine per 100 c.c. of the solvent. The solubility of iodine in *carbon disulphide*, which solidifies at —116°, is:

	—100°	—20°	0°	10°	20°	25°	30°	42°
Iodine .	0·32	1·14	7·89	10·51	14·62	16·92	19·26	26·75 per cent.

A. A. Jakowkin's number at 25° is 23·0 grms. of iodine per 100 c.c. of sat. soln. corresponding with 15·4 grms. of iodine per 100 grms. of soln. H. Arctowsky found

100 grms. of a sat. soln. of bromine in carbon disulphide contained 45·4 grms. of bromine at −95°, 39·0 grms. at −110·5°, and 36·9 grms. at −116°. S. U. Pickering, P. Wäntig, and J. Ogier obtained the values −5·008, −5·241, and −4·8 Cals. for the mol. ht. of soln. of iodine in 12·780 mol. of carbon disulphide. The heat of soln. of iodine in carbon disulphide decreases from −17·65 to −16·65 cals. respectively for dil. and sat. soln. J. C. G. de Marignac found the sp. ht. 0·219 and 0·228 respectively for soln. of a gram-atom of iodine in 10 and 20 mol. of carbon disulphide. The soln. of bromine follow the additive law. The diffusion constant for iodine in carbon disulphide is 2·55 and of bromine 3·11 grms. per sq. cm. per day. The viscosity of a sat. soln. of bromine in carbon disulphide is 0·00378 (16°), and of iodine 0·00378 at 16°. According to A. Harion, the refractive index of a 0·2 per cent. soln. is 2·074 for the *D*-line, and 1·982 for the *G*-line, if the soln. follow the additive rule. There is anomalous dispersion. The absorption spectrum of a soln. of bromine in carbon disulphide is not that which characterizes liquid bromine. The soln. are non-conductors of electricity. The colour of the soln. like the vapour is purple in thin layers, blue in thick layers.

A sat. soln. of iodine in *methyl iodide* has a sp. gr. of 3·548 at 23°; the solubility increases with rise of temp. and the mixture appears to be completely miscible above the m.p. of iodine. The absorption coeff. of chlorine in *carbon tetrachloride*, is 83 at 0°, and as measured by W. J. Jones at 15°, 51·7. According to L. Bruner and H. Arctowsky, the solubility of iodine in carbon tetrachloride at 14·8° is 20·6 grms. per litre, and at 25°, 30·33 grms. per litre. The soln. do not conduct electricity appreciably, and according to S. U. Pickering the mol. ht. of soln. is −5·782 per 700 mol. of water. According to W. Herz and M. Knock, the solubility of iodine in an aq. soln. of *glycerol* of sp. gr. 1·2555 at 25° (water at 4° unity) and containing about 1·5 per cent. of impurities, is :

Glycerol . .	0	7·15	20·44	40·95	69·2	100 per cent.
Iodine . .	0·0304	0·0342	0·0482	0·0875	0·278	1·223 ,, ,,
Sp. gr. . .	0·9979	1·0198	1·0471	1·0995	1·1765	1·2646

P. Walden[34] has studied soln. of iodine in *acetaldehyde*, *hydrazine hydrate*, and *acetonitrile*; J. H. Mathews, soln. of iodine in *pyridine*, *ethyl*, *allyl*, and *phenyl isothiocyanic esters*, and *phenyl isocyanate*; while H. A. Allen has studied soln. of bromine and iodine in various *oils*.

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§ 12. Chemical Reactions of Chlorine, Bromine, and Iodine

Chlorine unites directly with most of the elements. The inert gases of the argon family, nitrogen, oxygen, and some of the platinum metals, resist attack by free chlorine, although compounds with all but the inert gases can be obtained indirectly. Chlorine unites directly with **hydrogen** in light, but not in darkness; the union is also induced by the silent electrical discharge, or by the mere presence of some catalytic agents. Chlorine is not combustible in air. A jet of burning hydrogen lowered into a jar of chlorine continues burning with the formation of hydrogen chloride. Conversely, chlorine gas may be burnt in an atm. of hydrogen. Hydrocarbons are decomposed by chlorine; for instance, a piece of cotton wool soaked in warm turpentine ($C_{10}H_{16}$) will inflame when placed in a jar of chlorine. The burning of the turpentine in chlorine gas is accompanied by the separation of dense clouds of free carbon; the chlorine combines with the hydrogen forming hydrogen chloride. A wax candle burns in chlorine with a very smoky flame; the hydrocarbon—wax—is decomposed in a similar manner. Hence, chlorine may be regarded as non-combustible, and a supporter of combustion. Hydrogen and bromine unite under the influence of the silent discharge or when heated, but not when exposed to sunlight. Hydrogen and iodine unite when heated; at ordinary temp. the reaction with hydrogen and iodine is endothermal, being −0·8 Cals., but the reaction is exothermal above about 500°.

In 1842, T. Andrews[1] pointed out that although moist chlorine combines energetically with zinc, copper, and iron-filings, perfectly dry chlorine "has no action whatever at ordinary temp.. . . . and the same remarks may be applied to the behaviour of dry bromine in contact with dry metals." Indeed, thoroughly dry chlorine is somewhat inert chemically, and it has no appreciable action upon bright metallic sodium, copper, etc. Dried chlorine scarcely acts at all upon dry silver;

moist chlorine readily attacks the metal, more rapidly in light than in darkness. Moist chlorine is particularly reactive towards these solids. No one has succeeded in drying **mercury** and chlorine so thoroughly that the two elements do not react at ordinary temp. Chlorine does not combine with **oxygen** directly, although several compounds of chlorine and oxygen can be obtained indirectly forming a series of chlorine oxides or hydroxy-chlorine compounds. While the affinity of the halogens for hydrogen decreases with increasing at. wt., the general tendency with oxygen is in the reverse direction, but not in so marked a way as with hydrogen. Thus, although fluorine forms no known compound with oxygen, numerous compounds of oxygen with chlorine have been obtained; and, judging by the known compounds with oxygen, the affinity of bromine for oxygen appears to be less, not greater, than is the case with chlorine. Bromine seems to occupy an anomalous position with respect to oxygen, although it must be remembered that bromine has not been investigated so much as chlorine. Bromine and iodine form an unstable series of compounds analogous with hypochlorites and chlorates, but the bromine analogue of perchlorates has not been prepared. To summarize:

	Fluorine.	Chlorine.	Bromine.	Iodine.
Oxidizing action . .	Strongest	Very strong	Strong	Weak
Oxy-acids . . .	None	$HClO$	$HBrO$	HIO
		$HClO_2$	—	—
		$HClO_3$	$HBrO_3$	HIO_3
		$HClO_4$	—	H_5IO_6
Oxides . . .	None	Cl_2O	—	—
		ClO_2	—	I_2O_4
		—	—	I_2O_5
		Cl_2O_7	—	—

P. Hautefeuille and J. Chappius[2] claim to have made a compound, $N_2Cl_2O_{18}$, by the action of the silent electrical discharge on a mixture of chlorine and oxygen with a trace of nitrogen. The affinity of bromine for oxygen seems to be even less than that of chlorine or iodine for oxygen. No bromine oxides are known, but several oxides of chlorine and iodine have been made. According to M. Berthelot,[3] no change could be detected after exposing iodine in an atm. of oxygen to sunlight for five months; but J. Ogier obtained a compound of the two elements under the influence of the silent discharge.

The rapidity of the action of the halogens on **water**, previously discussed, is slower the greater the at. wt. of the halogen. Moist chlorine, or chlorine water, is a powerful oxidizing agent. The decomposition of chlorine water in sunlight has already been discussed, whereby oxygen gas is given off and hydrogen chloride is formed: $2H_2O+2Cl_2 \rightleftharpoons 4HCl+O_2$. This reaction is reversible in light, and even a conc. aq. soln. of hydrochloric acid is oxidized by air in light, so that such a soln. acquires a yellow colour owing to the formation and soln. of free chlorine formed by reaction with the absorbed oxygen. W. Henry[4] also found, in 1800, that when a mixture of hydrogen chloride and oxygen is passed over platinum black, the mixture is decomposed with the formation of chlorine and water: $4HCl+O_2=2H_2O+2Cl_2$, and it has also been shown that the metals, iridium, palladium, ruthenium, and osmium act in a similar way.

The heat of formation of a molecule of water is 68·4 Cals. and of a molecule of hydrogen chloride in aq. soln., 39·3 Cals. Hence, in the reaction $H_2O_{aq.}+Cl_{2aq.}=2HCl_{2aq.}+O$, the amount of heat required to decompose a molecule of water is nearly 10 Cals. less than that evolved in the formation of two molecules of hydrogen chloride in aq. soln. Hence, the instability of a soln. of chlorine in water might have been anticipated from the thermochemical data. If, however, the gases be in question: $2HCl_{gas}+O=H_2O_{gas}+Cl_{2gas}+13·0$ Cals., and this agrees with observation, for the reaction once started will proceed to a certain limiting value without further heating if sufficient precautions be taken to prevent loss of heat by radiation. This reaction is the basis of Deacon's process for chlorine.

If a piece of coloured litmus paper, coloured petals of a flower, or a piece of cloth dyed with turkey red or indigo blue be placed in a jar of dry chlorine no appreciable change occurs; but if moisture be present, the colours are bleached by the chlorine. The action appears to be due to the formation of a colourless oxidation product. Ordinary oxygen will not do the work of bleaching. One school of chemists therefore assumes that the oxidation is effected by the nascent oxygen. A soln. of indigo is decolorized by chlorine and bromine; and a soln. containing a milligram of diphenylamine in 10 c.c. of sulphuric acid is coloured an intense blue.

The direct union of many of the **metals** with chlorine is attended by incandescence—*for instance*, powdered antimony, arsenic, and bismuth when shaken into a flask containing chlorine. Since the chlorides of antimony, etc., so formed are poisonous, the experiments are best made in a closed vessel, or in a well-ventilated fume chamber. When the bulb tube containing the powdered element is raised, it is easy to shake the contents through the flask of chlorine to illustrate the incandescence which attends the combustion, without an escape of the poisonous chlorides into the atm. of the room. **Copper,** or **brass** foil—Dutch metal—**phosphorus, boron,** and **silicon** also ignite spontaneously in chlorine. Molten **sodium,** hot brass wire, and **iron** wire also burn in chlorine. Liquid chlorine at its b.p., -33.6°, reacts with **arsenic** with incandescence, but it does not react with **antimony** or **bismuth.** Arsenic even reacts with liquid chlorine at as low a temp. as -80° when potassium and sodium retain their metallic lustre without reaction. **Aluminium** takes fire in chlorine at -20°, but is not attacked at -33.6°. G. Just and F. Haber found that there is an emission of electrons as evidenced by electrical conductivity when the vapour of iodine acts on the heated metals, aluminium (160°), copper, and silver. Yellow phosphorus unites with liquid chlorine with explosive violence, and red phosphorus is also attacked. **Tin** and **gold** are also attacked by the liquid. According to G. Lunge, liquid chlorine does not attack iron below 90°, and it is on account of this inertness of iron that it is possible to transport large masses of liquid chlorine in iron bombs. Chlorine gas attacks finely divided gold at ordinary temp.,[5] bromine quickly dissolves gold; dry iodine does not attack gold, but between 50° and the m.p. of iodine, gold forms crystals of aurous iodide, AuI. **Platinum** is attacked by chlorine under certain conditions. According to F. Haber, if a platinum electrode be dipped into hydrochloric acid containing chlorine, and then thoroughly washed with water and hot alkali, a blue coloration appears in contact with starch and potassium iodide, which is much more intense than that produced by the catalytic action of the metal on the oxygen of the air, and it is considered that the metal has been attacked. Platinum does not react with bromine either in aq. or in hydrochloric acid soln. Chlorine, bromine, or iodine, moist or dry, rapidly attacks **mercury.**[6] **Sodium** is indifferent towards bromine or iodine. According to V. Merz and W. Weith[7] no reaction occurs even at 300°. A piece of sodium was kept in contact with bromine for sixteen years without chemical action. With **potassium** and bromine or iodine the reaction occurs with explosive violence. **Magnesium** foil is not attacked after lying for five years in contact with bromine, but **aluminium** is rapidly attacked by bromine with incandescence.

Sulphur reacts with liquid chlorine in the proximity of its b.p., and it forms various chlorides of sulphur; similarly with **selenium** and **tellurium**; at lower temp. the liquid does not react with sulphur, while it does react with selenium and tellurium. Liquid chlorine reacts with **sulphur dioxide** forming sulphuryl chloride, SO_2Cl_2; **carbon disulphide** is miscible in all proportions with liquid chlorine without chemical action. All **hydrogen compounds,** excepting hydrogen fluoride, are decomposed by chlorine with the formation of hydrogen chloride—*e.g.* hydrogen sulphide, hydrogen phosphide, arsenide, iodide, etc. The metal **bromides, iodides,** and **sulphides** are likewise decomposed either at ordinary or at higher temp. According to M. Berthelot,[8] bromine is absorbed by conc. hydrochloric or aq. soln. of barium or strontium chlorides with the development of much heat—owing, he assumes, to the formation of a perchlorobromide, $R''(Cl.Br_2)_2$. N. N. Beketoff observed

no action between iodine and cæsium chloride after standing for 50 days at room temp.

In their study of the action of iodine on **sodium thiosulphate** in 1842, M. J. Fordos and A. Gélis [9] found that a soln. of iodine is decolorized by this salt, owing to the formation of sodium tetrathionate, $Na_2S_4O_6$, and sodium iodide: $I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$. H. Hertlein translates this reaction in terms of the ionic hypothesis: $4Na^{\cdot}+2S_2O_3''+I_2=4Na^{\cdot}+2I'+S_4O_6''$, where the two negative S_2O_3'-anions transfer half their charge to the un-ionized iodine atoms forming two I'-ions, and the two S_2O_3''-ions simultaneously form one S_4O_6''-ion. According to C. A. R. Wright (1870) and S. U. Pickering (1880), there is a secondary reaction resulting in the formation of sodium hydrosulphate. The latter represented the reaction: $Na_2S_2O_3+4I_2+5H_2O=8HI+2NaHSO_4$, and the soln. becomes distinctly acid; C. A. R. Wright attributed the formation of the sulphate to the oxidizing action of iodine on the tetrathionate, say: $Na_2S_4O_6+7I_2+10H_2O=14HI+2H_2SO_4+2NaHSO_4$, and not to the direct oxidation of the thiosulphate. S. U. Pickering noted that a greater proportion of sulphate is formed the higher the temp.—at 0° about 1·84 per cent. of the iodine is consumed in forming sodium hydrosulphate; at 10°, 1·94 per cent.; at 20°, 2·10 per cent.; at 30°, 2·35 per cent.; at 52°, 3·90 per cent.—the degree of dilution, the excess of alkali iodide or the amount of hydrochloric acid, and the time occupied by the reaction do not affect the result. According to R. H. Ashley, the oxidation of the thiosulphate in alkaline soln. progresses further than the tetrathionate. G. Topf, J. P. Batey, E. Abel, C. Friedheim, and others have also noted the formation of sulphates during the action of iodine on sodium thiosulphate in alkali or sodium hydrocarbonate soln. I. M. Kolthoff thus summarized his observations: The tetrathionate reaction occurs in neutral and in strongly or feebly acidic soln., while in weakly alkaline soln. some sulphate is simultaneously formed, and in strongly alkaline soln. all the thiosulphate may be converted into sulphate. The decomposition of the thiosulphate in a strongly acid soln. is slow in comparison with the formation of tetrathionate. According to J. Bougault, in alkaline soln. the iodine forms a hypoiodite: $2NaOH+I_2=NaI+NaOI+H_2O$, which reacts with the thiosulphate: $Na_2S_2O_3+4NaIO+H_2O=2NaHSO_4+4NaI$; M. J. Fordos and A. Gélis, and G. Lunge have shown that the hypochlorites, hypobromites, and hypoiodites also oxidize the thiosulphate to tetrathionate. Some alkali iodate is also formed: $6NaOH+3I_2=5NaI+NaIO_3+3H_2O$. The oxidation to iodate is much retarded by using sodium hydrocarbonate, and still more by using normal carbonate in place of the hydroxide, and E. J. Maumené noticed that with barium thiosulphate, BaS_2O_3, other polythionates are formed—*e.g.* $H_2S_2O_4$ and $H_2S_6O_9$—as well as the tetrathionate. Chlorine and bromine act differently from iodine on the thiosulphates because, said H. Hertlein, the ionizing tendency of the two first-named halogens is so strong and the salt is oxidized to sulphate. According to M. Berthelot, the oxidation of sodium thiosulphate to the sulphate by bromine liberates 150 Cals. M. J. Fordos and A. Gélis noted that the sulphate is formed when chlorine or bromine acts on the thiosulphate: $Na_2S_2O_3+4Cl_2+5H_2O=Na_2SO_4+H_2SO_4+8HCl$. As shown by G. Lunge, the reaction takes place in two stages; there is first a considerable precipitation of sulphur: $Na_2S_2O_3+H_2O+Cl_2=2NaCl+H_2SO_4+S$; and the turbidity then clears owing to the oxidation of the sulphur to sulphuric acid: $S+4H_2O+3Cl_2=6HCl+H_2SO_4$. G. Lunge also noted that a little tetrathionate is formed: $2Na_2S_2O_3+Cl_2=2NaCl+Na_2S_4O_6$; and some trithionate is formed at the same time.

According to L. W. Andrews,[10] when **potassium iodide** is titrated with chlorine water in neutral soln. with chloroform or carbon tetrachloride as indicator (these immiscible solvents become violet, owing to the liberation of iodine, and they become colourless when titration is complete), the reaction is represented: $KI+3Cl_2+3H_2O=KCl+HIO_3+5HCl$. This reaction is the basis of A. and F. Dupré's process for titrating potassium iodide (1855). If a large excess of hydrochloric acid be present,

the reaction stops at an earlier stage for the ensuing reaction is symbolized: $KI+Cl_2=KCl+ICl$, and the iodine chloride colours the liquid yellow. If a soln. of potassium iodate be used in place of chlorine water in titrating potassium iodide the stage at which the reaction stops depends upon the conc. of the acid; with low conc. the reaction goes no further than the liberation of the iodine: $5KI+KIO_3+6HCl=6KCl+3I_2+3H_2O$; with an excess of acid, $2KI+KIO_3+6HCl=3KCl+3ICl+3H_2O$.

In J. L. Gay Lussac and L. J. Thénard's early attempt [11] to decompose oxymuriatic acid (chlorine) by passing it over red-hot **charcoal**, they reported:

> The first portions of the oxygenated muriatic gas were completely converted into ordinary muriatic gas. This effect diminished gradually in spite of a very great elevation of temp., and soon the gas passed without alteration, mixed only, towards the end of the experiment, with one thirty-third of an inflammable gas, which we believe to be carbonic oxide gas. This result clearly showed us that oxygenated muriatic gas is not decomposed by charcoal, and that the muriatic gas which we had obtained at the commencement of the operation was due to the hydrogen of the charcoal. . . . In fact, on taking ordinary charcoal without igniting it, muriatic gas was disengaged during a lengthened period even at a temp. only slightly elevated. . . . According as the charcoal lost its hydrogen, however, the quantity of muriatic acid went on diminishing, and finally nothing was obtained but oxygenated muriatic gas (*i.e.* chlorine).

En passant, this is one of the best ways of purifying charcoal. H. Davy (1814) [12] and H. Züblin (1881) obtained no evidence of a reaction between iodine or bromine and carbon at a white heat. Porous charcoal absorbs chlorine with the evolution of 6·78 Cals. per 35·5 grms. of chlorine. According to W. G. Mixter strongly compressed sugar charcoal absorbs about 4 per cent. of chlorine at a red heat, and does not give it up in vacuo at that temp. About 1·5 per cent. of bromine and traces of iodine are also absorbed by porous charcoal. The absorbed gas can be displaced by hydrogen but not by nitrogen; bromine and iodine are less easily absorbed and more easily lost than chlorine. Lampblack absorbs more chlorine than charcoal, and both lose the adsorbed gas at about 1000°. Chlorine seems to act with most energy on those forms of carbon which are contaminated with hydrogen. Gas carbon, graphite, and the diamond are not affected by chlorine. M. Meslans [13] found that if hydrogen be passed over the charcoal sat. with this gas, hydrogen chloride is formed in darkness; and according to M. Berthelot and A. Guntz, much chlorine is at the same time displaced by the hydrogen with an absorption of heat. The net result of the process is therefore an absorption of heat. If water be poured on carbon sat. with chlorine, both hydrogen chloride and carbon dioxide are formed. R. Lorenz found that chlorine is completely converted into hydrogen chloride and carbon monoxide by passing a mixture of steam and chlorine through a tube filled with coke at a dull red heat. The reaction, $Cl_2+H_2O+C=CO+2HCl$, is complete. If the hydrogen chloride be absorbed by water, the residual carbon monoxide is contaminated with but a little carbon dioxide. According to F. Fischer, coal rapidly absorbs 30–36 per cent. of bromine. The brominated coal gives off hydrogen bromide. Carbon unites with chlorine directly when the carbon forms an electric arc in an atm. of chlorine; hexachlorobenzene, $C_6H_6Cl_6$, is formed; and if the gas be confined in a vessel with a construction so that the upper compartment contains the arc, and the lower part is cooled by a freezing mixture, hexachloro-ethane, C_2Cl_6, is formed. The positive pole appears to be the active agent. Similar results were obtained with bromine and iodine. According to E. Barnes, dry chlorine has no perceptible action on **calcium carbide** after two months' treatment at ordinary temp. According to H. Moissan, and F. P. Venable and T. Clarke, bromine has no action in the cold on calcium carbide, but when heated the products are calcium bromide and carbon. E. Barnes, however, found that liquid bromine attacks calcium carbide at ordinary temp. producing carbon hexabromide and calcium bromide: $CaC_2+4Br_2=CaBr_2+C_2Br_6$; at 100° in sealed tubes, carbon and calcium bromide but no carbon hexabromide were formed. E. and H. Erdmann found that iodine acts on calcium

carbide at 170°, producing tetra-iodoethylene and di-iodoacetylene. R. Lucion (1889) could find no evidence of a reaction between dry **carbon dioxide** and chlorine at a red heat, but in the presence of moisture, hydrogen chloride is formed. Chlorine unites with **carbon monoxide** forming phosgene, or carbonyl chloride, $COCl_2$.

Ammonia reacts vigorously with chlorine, forming ammonium chloride and nitrogen gas; if the chlorine be in excess, oily drops of violently explosive nitrogen chloride, NCl_3, are formed. Some ammonium hypochlorite, NH_4OCl, is simultaneously produced. Nitrogen bromide does not appear to be formed by the action of bromine on aq. ammonia. The speed of the reaction, $2NH_3+3Br_2=N_2+6HBr$, is more rapid with free ammonia than with the ammonium salts, and S. Raich [14] attempted to get a comparison of the affinity coeff. of the acids forming the various ammonium salts in terms of the rate of decomposition of the different ammonium salts by bromine. It was assumed that the stronger the affinity of the acid for ammonia, the slower the rate of the decomposition of bromine. It was found that with the ammonium salts of the organic acids,—*e.g.* oxalic and formic acids—side reactions occurred owing to oxidation or substitution. With 10 c.c. of a $0.05N$-soln. of the ammonium salts, and 25 c.c. of a $0.075N$-soln. of bromine water at 25°, 2·5 c.c. of bromine was consumed in

	Hydrochloric	Nitric	Sulphuric	Arsenic	Monochloracetic	Tartaric	Acetic acid.
Time	162	148	118	98	29	20	4 hrs.

This was taken to represent the relative order of the affinity of these acids for ammonia. When an alcoholic soln. of iodine is treated with ammonia, substitution products and nitrogen iodide are formed. According to A. W. Browne and F. F. Shetterley,[15] a trace of azoimide, HN_3, is formed by the action of chlorine on acidic or alkaline soln. of **hydrazine sulphate;** according to E. Ebler, hydrazine sulphate or chloride in acid soln. is completely decomposed by bromine—for example: $N_2H_4+2Br_2=4HBr+N_2$. A soln. of iodine in potassium iodide acts in a similar manner. T. Curtius and H. Schulz found that tincture of iodine acts on an alcoholic soln. of **hydrazine hydrate** as symbolized by the equation: $5N_2H_4.H_2O+2I_2=4N_2H_4HI+5H_2O+N_2$. **Nitric oxide** unites with chlorine forming nitrosyl chloride, $NOCl$; the same product is formed when chlorine acts on **nitrogen tetroxide,** N_2O_4. Bromine also forms nitrosyl bromide, $NOBr$; but iodine suspended in water forms nitric and hydriodic acids. When iodine is warmed with conc. **nitric acid,** iodic acid and nitrogen peroxide are formed. According to J. B. Senderens, chlorine acts on **silver nitrate** forming silver chlorate and silver chloride, while according to H. Moissan,[16] chlorine free from hydrogen chloride precipitates silver chloride from a soln. of silver nitrate, and the corresponding amount of oxygen is set free. Iodine and silver nitrate form silver iodide and iodic acid. Solid iodine acts on silver nitrate in the dark in accord with the equation: $5AgNO_3+3I_2+3H_2O=5AgI+5HNO_3+HIO_3$; and bromine, $AgNO_3+Br_2+H_2O=AgBr+HOBr+HNO_3$, as indicated by J. Spiller, and C. F. Schönbein. According to K. Brückner, **mercurous oxide,** Hg_2O, and iodine, I_2, in the proportions 1 : 2 mol. react: $6Hg_2O+12I_2=11HgI_2+Hg(IO_3)_2$; the same transformation occurs slowly in the presence of water, more rapidly in hot water. With a dry mixture of mercuric oxide, HgO, and iodine, $6HgO+6I_2=Hg(IO_3)_2+5HgI$. The action of the halogens on the alkaline hydroxides is discussed in connection with the oxy-chlorine acids. In the presence of **hydrogen peroxide** and an alkali hydroxide, the alkali chloride is formed: $Cl_2+H_2O_2+2KOH=2KCl+O_2+2H_2O$. Similarly with iodine and bromine. When near its b.p. liquid chlorine reacts with **arsenic** forming arsenic trichloride, but at lower temp. arsenic and **antimony** are not affected. **Alkali arsenites** are oxidized to arsenates: $K_3AsO_3+H_2O+Cl_2=KH_2AsO_4+2KCl$. **Ferrous salts** are oxidized to ferric salts: $6FeSO_4+3Cl_2=2Fe_2(SO_4)_3+2FeCl_3$. Alcohol, ether, chloroform, and carbon disulphide are better solvents for bromine or iodine than water, so that if a soln. containing free bromine or free iodine is shaken up with one of these solvents, the former colours these solvents yellow or brown, and the latter rose to reddish-violet, according to the concentration. Liquid chlorine at

its b.p. does not react with **potassium permanganate; thallous chloride** is converted into Tl_2Cl_3 by liquid chlorine, and into Tl_2Cl_4 by gaseous chlorine at ordinary temp.

Uses of the halogens.—Chlorine is largely employed in the preparation of bleaching powder or chloride of lime, bleaching liquor or hypochlorites, chlorates, and various chlorinated chemicals—*e.g.* 3000 tons of chloracetic acid are said to be used per annum in the manufacture of synthetic indigo; chloral; carbon tetrachloride; various chlorinated ethanes are used in the extraction of fats, etc., with the advantage of their being non-inflammable; chloro-derivatives benzene and naphthalene, in the manufacture of dyes. Liquid chlorine was formerly employed in the chlorination process for gold, but this has been largely displaced by the cyanide process. The gas was introduced by the Germans as an agent of destruction in warfare in the second battle of Ypres, on 23rd April, 1915. This was in contravention of International agreement. The Germans thus obtained a temporary advantage until respirators with sodium thiosulphate and carbonate had been supplied to the Allied Forces, and in self-defence, the Allies had retaliated on the Germans with interest in kind. In consequence, this and other gases even more deadly were used on the battlefields. For chlorine poisoning the inhalation of hydrogen sulphide, or of the vapour of alcohol, ether, chloroform, or steam has been recommended. There is a form of chlorine poisoning to which the workmen dealing with electrolytic chlorine are subject;[17] it is attended by swellings in various parts of the body, giddiness, and coughing; the effects are supposed to be due not to the direct action of chlorine, but rather to the action of chlorine oxides contained in the gas. According to A. Leymann, the workmen may also be affected by a peculiar skin disease which has been traced to chlorinated products derived from the action of chlorine on the tar coating of the electrolytic cells used in making the gas.

At the beginning of the nineteenth century, chlorine was recommended as a disinfectant by W. Cruickshank;[18] and towards the middle of the century, the efficiency of chlorinated lime as a disinfectant and deodorant was generally recognized, and in 1854 a Royal Commission recommended this substance for deodorizing the sewage of London. At that time, the action of disinfectants was generally supposed to be effected by the arresting or preventing of putrefactive changes. The work of T. Schwann (1839), L. Pasteur (1862), etc., showed that bacteria were responsible for putrefaction and fermentation, and that specific organisms were responsible for certain specific diseases. Chlorine was successfully used in the sanitary work connected with the outbreak of puerperal fever in Vienna in 1845. J. Race estimated that in 1918 over 3000×10^6 gallons of water were being treated per diem in North America; and over 1000 cities and towns employed the process.

In 1889, W. Webster proposed the use of electrolyzed sea-water as a disinfectant, and this liquid was introduced by E. Hermite (1889) as *Hermite's fluid* for domestic purposes as well as for flushing sewers and latrines. The objections to this liquid were due to the unstable character of the magnesium hypochlorite formed at the same time as the sodium hypochlorite in the electrolysis of sea-water. The magnesium salt readily hydrolyzes, forming the hydroxide which deposits in the electrolytic cell, and leaves a soln. of unstable hypochlorous acid. A conc. soln. of sodium chloride was soon substituted for sea-water, and the liquor has been called *electrozone, chloros,* etc. Various preparations of hypochlorites were also employed on a large scale for the purification of water; H. Bergé used chlorine peroxide; and in A. C. Houston's process water was chlorinated with chlorine itself.

S. Rideal noticed the peculiar effect of ammonia on the germicidal value of hypochlorites; he said that the first rapid consumption of chlorine is succeeded by a slower action which continues for days, and that the germicidal action continues after free chlorine and hypochlorite have disappeared; it appeared that ammonia substitution products are formed yielding compounds more or less germicidal.

J. Race, attempting to make *ammonium hypochlorite* by the double decomposition of ammonium oxalate and calcium hypochlorite, obtained a soln. with its germicidal action greatly enhanced; and it was assumed that the unstable ammonium

hypochlorite passed into monochloroamine, $NH_4OCl=NH_2Cl+H_2O$. The use of chloroamine for chlorinating water was tried on a large scale at Ottawa (1917), and at Denver, Col. (1917), with good results. N. D. Dakin and co-workers (1917) tried other chloroamines—*e.g.* sodium toluene-*p*-sulphochloramide; and several aromatic sulphodichloroamines, *e.g.* $Cl_2N.SO_2.C_6H_4.COOH$, were found suitable for use in tabloid form for the sterilization of small quantities of water by cavalry and other mobile troops. The preparation has the trade name *halazone*, and H. D. Dakin and co-workers have shown that three parts of halazone per million suffice to sterilize heavily polluted waters in 30 min., and this concentration is effective in destroying pathogenic organisms. The effect of ammonia in destroying the bleaching activity and the property of oxidizing organic matter by hypochlorite soln. is taken to prove that the nascent oxygen hypothesis fails to explain the retention of the bactericidal power of such soln., and it is attributed to the direct toxic action of chlorine or chloroamines.

Bromine is used in the preparation of various chemicals—bromides, etc.—employed in the manufacture of aniline dyes, and in photography. The alkali bromides are used medicinally, and free bromine is used as an oxidizing agent in analytical chemistry; in the manufacture of ferricyanides, permanganates, etc. Bromine is also used as a disinfectant or sterilization agent, largely in the form of *bromum solidificatum*, which is a mixture of kieselguhr with a binding agent which is moulded in the form of rods, baked, and sat. with liquid bromine. The product contains up to 75 per cent. of its weight of bromine.[19]

Iodine is used in various forms in medicine—*e.g.* tincture of iodine, liquor iodi, iodized cotton, iodized wine, iodized water, oils and syrups; iodides of potassium, mercury, iron, arsenic, lead, etc.; and as methyl iodide or di-iodide; iodoform, CHI_3; ethyl iodide, C_2H_5I; iodole, $C_4I_4.NH$; aristole; etc.—largely for external application as an antiseptic. Some iodides are used in photography, and in analytical operations; and a considerable amount of iodine is used in the preparation of aniline dyes.

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§ 13. Colloidal Iodine and Iodized Starch

W. Harrison [1] prepared unstable **hydrosols of iodine** by adding hydriodic acid to a dil. soln. of iodic acid; and by adding alcohol to soln. of iodine in glycerol. The hydrosol is at first blue, but it quickly flocculates forming a grey aggregate which, if the conc. be small, can scarcely be recognized. J. Amann has prepared soln. in sulphuric acid and in propylamine. The relation between the colour and the nature of the solvent has already been discussed.

Dry iodine does not colour dry starch blue, but rather turns it brown, and the brown gives place to blue on contact with water. When in contact with starch, iodine forms an intense blue-coloured product, **iodized starch.** Under similar conditions, bromine forms an intense yellow. According to C. Meineke, the reaction with iodine is delicate enough to reveal the presence of 0·0000003 grm. of iodine per c.c., while F. Mylius and G. Just say 0·0000001 grm. The great sensitiveness of this reaction makes starch a valuable indicator for the presence of free iodine in volumetric analysis. According to F. C. Accum, starch was recommended for the detection of iodine by F. Stromeyer. F. Mylius, F. E. Hale, and C. Lonnes found that hydrogen iodide and iodine are present in iodized starch in the ratio 1 : 4, and the formula $(C_{24}H_{40}O_{20}I)_4HI$ was assigned to the blue product where the iodine and iodide are related as $H-I\equiv I_4$, etc. F. Seyfert and J. Tóth objected to F. Mylius' contention that an iodide or hydriodic acid is necessary for the production of the blue coloration. An excess of potassium iodide colours iodized starch brown, the brown colour becomes blue on dilution with water. The reddish-brown colour produced by the action of iodine and a conc. soln. of potassium iodide on starch is also turned blue by water. F. Mylius suggested that the reddened starch contains no potassium iodide, but twice as much iodine as the blue product, but F. E. Hale suggested that since a conc. soln. of potassium iodide turns the blue starch red, and the reddened product becomes blue when treated with water, it is more likely that the red product contains more iodide than the blue. According to E. W. Washburn, the presence of alkali chlorides, magnesium sulphate, etc., does not interfere. The colour obtained in the presence of potassium iodide is not the same in tint as if other salts are present; and the amount of iodine required to produce a blue colour of

the same intensity is smaller with soln. of potassium iodide than with soln. of other salts of the same conc. F. Mylius maintains that the presence of an iodide, *i.e.* 1 soln of a conc. at least 10^{-6} grm. per litre, is necessary for the development of the blue colour, so that the starch soln. is usually mixed with an iodide—say iodide of potassium, zinc, etc. C. Tomlinson found many other iodides served the same purpose.

According to W. Harrison, the addition of alcohol changes the blue colour of iodized starch to violet, red, orange, and yellow, and E. Baudrimont found that the same colour changes are produced by heat, provided not too much iodine is present. The blue colour begins to leave aq. iodized starch at about 4°, and disappears between 60 and 70°. A soln. of iodized starch heated above 70° is colourless if dil., and straw yellow if conc. On cooling, the original colour is restored if the soln. be rapidly heated and quickly cooled, but with a prolonged heating, the intensity of the colour is feebler, and maybe does not return at all. The colourless product is supposed by L. Bondonneau, J. L. P. Duroy, and P. Guichard to be a colourless organic iodide because the colour is restored by the addition of nitric acid or an iodate; and with chloroform, it becomes violet. L. W. Andrews and H. M. Göttsch say that clear starch soln. prepared at 150°, takes up in the cold iodine eq. to $(C_6H_{10}O_5)_{12}I$; a starch soln. heated with an excess of iodine to 100° for a short time forms $(C_6H_{10}O_5)_{12}I_2$; and a starch soln. heated to 100° for a long time gives a colourless soln. containing most of the iodine as an organic iodide; some hydriodic acid and glucose are also formed. F. Mylius and F. W. Küster say that dried blue-iodized starch forms a brown powder which becomes blue again in presence of water. The colour of iodized starch is so different from that of other iodine compounds that it has attracted some attention. N. Blondlot, A. Béchamp, J. J. Pohl, R. Fresenius, E. Duclaux, B. Brückner, and F. W. Küster have supported the hypothesis that iodized starch is a mixture of starch and iodine, or a soln. of the latter in the former, while E. G. Rouvier, A. Payen, J. Fritzsche, L. Bondonneau, P. Guichard, E. Sonstadt, H. Pellet, and F. Mylius hold it to be a chemical compound of starch and iodine, and hence arose the term **starch iodide.** There is, however, no agreement as to the composition of the alleged compound since the amount of iodine is variously reported to be from 3·2 to 19·6 per cent., and the formulæ accordingly extend over a wide range. A. Coehn showed that iodized starch is a negative colloid. F. W. Küster found the amount of iodine absorbed by solid starch is wholly dependent on the conc. of the soln., and he concluded that iodized starch is neither a compound nor a mixture, but is a well-defined solid soln. of iodine in starch. M. Katayama also showed that, in dil. soln., the conc. of the iodine in the starch is proportional to the conc. of iodine and starch respectively, but varies in a somewhat complicated manner with the iodide conc. In very dil. soln., it is proportional to the second or third power of the iodide conc., but the effect is proportionately smaller as the conc. increases, and depends also on the starch conc. He also draws a similar conclusion to F. W. Küster, L. W. Andrews, and H. M. Göttsch. Soln. of iodized starch give up considerable amounts of iodine to chloroform, but subsequent additions of chloroform give no sign of a partition coeff. as would be anticipated if the iodine were merely dissolved in the starch. The vap. press. of iodine in iodized starch is very small after the removal of the first portion of iodine. M. Padoa and B. Savarè measured the conductivities of soln. of iodized starch, and although it was not possible to obtain a product with a constant ratio between iodine and hydrogen iodide, they say that one definite additive compound, analogous with F. W. Küster's assumption, is formed. W. Biltz also argued that other substances are coloured blue by the adsorption of iodine. For example, A. Damour, R. J. Meyer, and N. A. Orloff found this to be the case with lanthanum acetate, and basic praseodymium acetate; C. Graebe also found euxanthic acid, cholic acid, and narceine behave similarly. Iodine is also adsorbed by a number of other substances forming brown instead of blue solid soln.—*e.g.* J. Walker and S. A. Kay found such to be the case with magnesia; W. A. R. Wilks

found that with slaked lime bromine and iodine dissolved in carbon tetrachloride form adsorption products, while chlorine forms a chemical compound. K. Estrup and E. B. Anderson studied the adsorption of iodine by precipitated barium sulphate; and H. Siegrist and E. Filippi found tannin and a number of organic bases to behave similarly. G. C. Schmidt studied the partition of iodine between alcohol and animal charcoal, and found that this is not in accord with Henry's law C/C_s=constant, where C denotes the quantity of iodine adsorbed by the charcoal, and C_s the quantity which remains in 10 c.c. of the solvent. O. C. M. Davis studied the partition of iodine with different solvents and with different forms of charcoal, and found that with constant surface area, the amount of adsorption is specific, depending both on the nature of the solvent and of the adsorbent. If x denotes the amount of iodine adsorbed when w grms. of solid are employed, the amount adsorbed per gram is represented fairly well by H. Freundlich's empirical formula: Amount adsorbed per gram x/w β, p, where β and p are constants. O. C. M. Davis found that

Solvent.	Animal charcoal. β	Animal charcoal. p	Sugar carbon. β	Sugar carbon. p	Cocoanut carbon.
Toluene	0·370	3·36	0·357	2·48	0·021
Benzene	0·382	3·22	0·302	2·49	0·018
Ethyl acetate	0·430	3·26	0·315	2·87	0·010
Alcohol	0·466	3·09	0·258	2·40	0·014
Chloroform	0·545	2·98	0·479	5·13	0·020

The adsorption of iodine is approximately the same with animal and sugar charcoal, but cocoanut charcoal adsorbs only a fraction of this amount. The adsorption consists of a surface condensation, and a diffusion, owing to solid soln., into the interior; the surface condensation is complete in a few hours, the diffusion may occupy weeks or months. The product obtained by saturating animal charcoal with iodine has been used as a medicament under the trade name *iodantraco*, and L. Corridi has investigated which solvents extract the iodine most readily—water is slow, dil. acids are slower, but dil. alkali soln. extract most of the iodine. K. Scheringe and P. Guichard have studied the adsorption of iodine vapour by sand, silica, opal, agate, alumina, magnesia, beryllia, and charcoal. E. F. Lundelius has also studied the adsorption of iodide from soln. in carbon tetrachloride, carbon disulphide, and chloroform by charcoal.

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§ 14. The Atomic Weights of Chlorine, Bromine, and Iodine

The first determinations of the at. wt. of chlorine were obtained by the analysis of the chlorates; later determinations have been directed towards the quantitative synthesis of hydrogen chloride, or to the use of physical methods—mol. vol., limiting densities, and critical data. General calculations have been made by F. W. Clarke, B. Brauner, and others.[1]

I. The analysis of the chlorates. In 1826, J. J. Berzelius[2] determined the at. wt. of chlorine by the analysis of the chlorate. He determined the percentage amount of potassium chloride remaining after the ignition of the chlorate; he took the precaution to correct his result for the amount of solid mechanically carried away by the current of oxygen gas, or actually volatilized. This furnished the *ratio potassium chloride : oxygen*; J. J. Berzelius had previously determined the *ratio of silver : chlorine* in silver chloride by treating a soln. formed by dissolving a known weight of silver in nitric acid and precipitating silver chloride, or evaporating the soln. with hydrochloric acid. Hence, the precipitation of silver chloride by the addition of a known amount of potassium chloride to silver nitrate enables the *potassium : chlorine ratio* to be determined. The results allowed the relation between oxygen, potassium, chlorine, and silver to be computed.

The oxygen in the chlorates was determined by F. Penny (1839)[3] and by A. Stähler and F. Meyer (1911) by treating potassium, sodium, or silver chlorate with conc. hydrochloric acid: while T. J. Pelouze (1842), J. C. G. de Marignac (1842), C. Gerhardt (1845), L. Maumené (1846), V. Faget (1846) and J. S. Stas (1865) heated the chlorate according to the Berzelian process. J. C. G. de Marignac also made some experiments on potassium perchlorate in 1842; and T. W. Richards and H. H. Willard (1910) treated lithium perchlorate in an analogous manner. F. W. Clarke's calculation of the general mean of the experiments gave 60·846 ± 0·00038 parts of KCl from 100 parts of $KClO_3$.

The silver : chlorine ratio was determined by E. Turner (1829).[4] F. Penny (1839), J. C. G. de Marignac (1842), J. B. A. Dumas (1860), J. S. Stas (1865), and by T. W. Richards and R. C. Wells (1905) by the precipitation of silver chloride. L. Maumené reduced silver chloride to the metal by heating it in a stream of hydrogen; and J. S. Stas also synthesized silver chloride by heating the metal in chlorine gas. This ratio has also been determined by several less direct methods. F. W. Clarke's calculations furnished 32·8606 ± 0·00031 for the general mean representing the amount of chlorine which combines with 100 parts of silver to form silver chloride.

Since J. J. Berzelius' work, the alkali chloride : silver ratio has been repeatedly measured, among others by J. C. G. de Marignac (1842),[5] L. Maumené (1846), J. S. Stas (1865), T. W. Richards and E. H. Archibald (1903), E. H. Archibald (1904), T. W. Richards and A. Staehler (1907), and by A. Thiel (1904), T. J. Pelouze (1845), J. C. G. de Marignac (1842); and J. S. Stas (1865), A. Scott (1901), and T. W. Richards, P. Köthner, and E. Tiede (1909) determined the ratio between ammonium

chloride and silver. J. S. Goldbaum electrolyzed a soln. of sodium chloride with a weighed silver anode and mercury cathode. Sodium as cation forms an amalgam, and the chlorine attaches itself to the silver of the anode, and the increase in weight represents the halogen content of the salt. A correction was made for the silver which dissolved from the anode. He obtained Cl=35·456, when referred to sodium 23·00. F. W. Clarke's calculation of the ratio Ag : KCl=100 : x furnished as a general mean 69·1138 ± 0·00011 for the amount of potassium chloride which unites with 100 parts of silver to form silver chloride; or 52·0163 ± 0·00018 parts of potassium chloride furnish 100 parts of silver chloride.

The first ratio gives the relation between the mol. wt. of oxygen as standard and the mol. wt. of potassium chloride; the second gives the relation between potassium chloride and silver; and the third the relation between silver and chlorine. J. S. Stas' work on at. wt. has been deservedly eulogized. For many years it was considered to be so near perfection as was possible to man. J. S. Stas seemed to have taken the most subtle precautions to exclude errors of manipulation, and to ensure the purity of his materials. He also followed the advice of J. J. Berzelius, or, in order to eliminate constant errors, he used materials from different sources, and followed many different paths in arriving at his results. Only when consistent values were obtained by different methods did he assume that the results were reliable. The following outline will give an idea of the plan of J. S. Stas' work:

1. *Determination of the relation between sodium chloride and silver.*—Ten samples of a known weight of purified silver were dissolved in nitric acid, and each was treated with purified sodium chloride. The excess of silver was determined volumetrically and the precipitated silver chloride was reduced to metallic silver and weighed. The best representative value of these determinations was: 54·2078 parts *of NaCl were required for* 100 *parts of silver.*

2. *Determination of the relation between chlorine and silver.*—Silver chloride was prepared from purified silver in several different ways: (1) By burning the metal at a red heat in chlorine gas; (2) by dissolving the silver in nitric acid, and precipitating silver chloride (*a*) with hydrogen chloride, (*b*) with hydrochloric acid, and (*c*) with ammonium chloride (in this process some silver chloride was lost in washing the precipitate). The best representative value of this work was: 132·8445 *parts of silver chloride was obtained from* 100 *parts of silver.* By calculation it follows (1) that 100 parts of silver combine with 132·8445 less 100=32·8445 parts of chlorine; (2) that 100 parts of silver combine with 52·2078 − 32·8445=21·3633 parts of sodium. Or,

$$Ag : Na : Cl = 100 : 21{\cdot}3633 : 32{\cdot}8445$$

3. *Determination of the relation between silver chloride and oxygen.*—This gives the relation between silver, sodium, and chlorine. If the relation between hydrogen or oxygen and any one of these elements be known, the at. wt. of these elements with respect to hydrogen or oxygen as standards follows directly. This relation can be determined by converting silver chlorate into silver chloride: $2AgClO_3 = 2AgCl + 3O_2$. A known weight of purified silver chlorate was decomposed by sulphurous acid: $AgClO_3 + 3H_2SO_3 = AgCl + 3H_2SO_4$. The chlorates were also decomposed by ignition. As a result it was found that 74·9205 *parts of silver chloride were equivalent to* 100 *parts of silver chlorate*; or 25·0795 parts of oxygen were eq. to 100 parts of silver chlorate; or 25·0795 parts of oxygen are eq. to 74·9205 parts of silver chloride.

Since $AgClO_3 = AgCl + 3O$, if O=16, it follows that the eq. wt. x of silver chloride must be 25·0795 : 8+16=74·9205 : x, where x=143·395. But 100 parts of silver are eq. to 32·8445 parts of chlorine, and hence 132·8445 parts of silver chloride will correspond with 132·8445 : 143·395=100 : x, or x=107·942 parts of silver. Similarly for chlorine, since 132·8445 parts of chlorine unite with 107·942 parts of silver, 143·395 parts of silver chloride will contain 35·453 parts of chlorine. Hence, if O=16, Cl=35·453. Again for sodium, 32·8446 parts of chlorine combine with

21·3633 parts of sodium, and hence 35·453 parts of chlorine unite with 23·0599 parts of sodium.

Hence, if O=16, the combining weights of silver, sodium, and chlorine are related as

$$Ag : Na : Cl = 107·942 : 35·453 : 23·0599$$

Similar experiments were made with halogens bromine and iodine, and the remarkable accuracy of J. S. Stas' work may be judged by comparing his 1865 values with those employed at the present day:

	Chlorine.	Bromine.	Iodine.	Silver.
Stas' 1865 values . .	35·457	79·955	126·850	107·93
International table, 1918	35·46	79·92	126·92	107·88

J. S. Stas also repeated the work with lithium, sodium, and potassium; incidentally, the value for nitrogen was determined. The values deduced in this way were:

	Potassium.	Sodium.	Lithium.	Nitrogen.
Stas' 1865 values . .	39·14	23·04	7·02	14·04
International table, 1918	39·10	23·00	6·94	14·01

The chief weakness in J. S. Stas' work arose (1) from the difficulties in manipulating the unusually large amounts of material employed in each determination, and (2) precipitating his compounds from too conc. soln. in order to keep down the bulk of the liquid. This led to the adsorption of relatively large amounts of the precipitant by his precipitates. Indeed, says T. W. Richards (1911),[6] the presence of residual water and the loss of traces of "insoluble" precipitates by dissolution during filtration, have perhaps ruined more at. wt. determinations than any other two causes unless indeed the adsorption of foreign substances by precipitates may be ranked as an equally vitiating effect. Much of Stas' work has been revised—chiefly by T. W. Richards and his co-workers—with the idea of providing for the small errors which affected Stas' work.

It may here be emphasized [7] that different results may be obtained by varying the method of calculating at. wt. The ratios actually measured are affected by unavoidable errors of experiment, and during the calculation these errors may be distributed over the several ratios concerned, or they may all accumulate upon that value last determined. Thus, in calculating the at. wt. of fluorine from the observed ratio, $CaF_2 : CaSO_4$, the errors of experiment are superposed upon the errors involved in obtaining the at. wt. of calcium and sulphur when oxygen 16 is the standard of reference. In the ideal case, the observed data should be so treated that the errors are properly distributed among the different weighings, and their influence reduced to a minimum. The mathematical operations are well understood, and the laboratory should furnish the necessary data.

II. The quantitative synthesis of hydrogen chloride.—H. B. Dixon and E. C. Edgar [8] prepared chlorine by the electrolysis of fused silver chloride and weighed it in the liquid form; hydrogen was prepared by the electrolysis of a soln. of barium hydroxide and weighed occluded in palladium. The hydrogen was burnt in a globe filled with chlorine, and the excess of chlorine determined by absorption in potassium iodide and titration of the liberated iodine with sodium thiosulphate. The mean of nine determinations was 35·463(H=1·00762). W. A. Noyes and H. C. P. Weber passed hydrogen weighed in palladium over heated potassium chloro-platinate. The loss in weight of the latter salt gave the weight of chlorine employed. The hydrogen chloride produced was also collected either by absorption in water, or condensed to a solid by cooling with liquid air. The mean of twelve determinations gave 35·452(H=1). E. C. Edgar then synthesized hydrogen chloride by weighing the hydrogen, chlorine, and hydrogen chloride. The latter was freed from the excess of chlorine condensed along with the hydrogen chloride by allowing the liquid to evaporate; passing the vapour through a quartz tube filled with mercury vapours;

and condensing the purified hydrogen chloride, back to a liquid, or dissolving it in water. Result, 35·461. R. W. Gray and F. P. Burt first determined the weight of a normal litre of hydrogen chloride to be 1·63885 grms.; they then passed the gas over heated aluminium, and measured the volume of the liberated hydrogen. Two volumes of hydrogen chloride gave 1·00790 vols. of hydrogen. With Morley's value for the density of chlorine, it was found that 36·4672 grms. of hydrogen chloride give 35·4594 grms. of chlorine, if the unit of hydrogen be 1·0078 grm. P. A. Guye and G. Ter-Gazarian's determination of the relative density of hydrogen chloride also gave 35·461 for the at. wt. of chlorine. J. Deutsch obtained a rather lower value.

III. The analysis of nitrosyl chloride.—P. A. Guye and G. Fluss [9] first distilled a known weight of purified nitrosyl chloride, NOCl, over heated silver—this retained the chlorine; it was then passed over heated copper—this retained the oxygen; and finally it was passed over metallic calcium—this retained the nitrogen. The sum of the weights of chlorine, oxygen, and nitrogen so determined was usually a little less—up to 0·0012 grm.—than the weight of the nitrosyl chloride employed. The mean value for chlorine gave 35·468.

IV. Physical methods.—Several physical methods have been employed for determining the mol. wt. of hydrogen chloride. The density of hydrogen chloride determined by R. W. Gray and F. P. Burt [10] was 1·62698 grms. for a normal litre; and 1·42762 for oxygen. Hence, with the mol. wt. of oxygen, 32, as the standard of reference, the mol. wt. x of hydrogen chloride is given by the proportion 1·42762 : 1·62698 = 32 : x, where x=36·469; with the at. wt. of hydrogen 1·0076, the at. wt. of chlorine is 36·469—1·0076=35·461. The compressibility coeff.—that is, the mean deviation of hydrogen chloride from Boyle's law—required for an application of the D. Berthelot's *method of limiting densities* (**1.** 6, 8), has been determined by A. Leduc to be $A_0{}^1$=0·00758; E. Briner, 0·00750; R. W. Gray and F. P. Burt, 0·00743; and A. Jaquerod and O. Scheuer found for oxygen $A_0{}^1$=0·00097; R. W. Gray and F. P. Burt, 0·000964. Hence, A. Leduc calculated the mol. wt. of hydrogen chloride to be 36·460; and E. Briner, 36·462. A. Leduc's *method of molecular volumes*, where it is assumed that all gases at corresponding temp. and press. have the same mol. vol., gave the value 36·450 for the mol. wt. of hydrogen chloride; and E. Briner, 36·453. The *method by the reduction of the critical constants*, based on the equation: Mol. wt. referred to oxygen 32 is equal to $22·412W/(1+a)(1-b)$, where W denotes the weight of a litre of gas at 0° and 760 mm., reduced to sea-level, and latitude 45°. P. A. Guye and G. Ter-Gazarian [11] found for a normal litre of hydrogen chloride, W=1·6398; and $(1+a_0)(1-b_0)$=1·00773, so that the mol. wt. of hydrogen chloride is 36·4393, and if the at. wt. of hydrogen is 1·0078, that of chlorine will be 35·4615.

Starting with oxygen 16 as the standard of reference, F. W. Clarke (1910) regards 35·4584 ± 0·0002 as the best representative value for the at. wt. of chlorine if the at. wt. of the silver be 107·880—0·00029; and B. Brauner (1913) considers the best representative value to be 35·457, if silver be 107·880; 35·456, if silver be 107·876; and 35·454, if silver be 107·871. B. Brauner also inquires: What reliance can be placed on the third decimal? and answers that the uncertainty is smaller if silver be regarded as a fixed basis with respect to oxygen 16, and greater when the at. wt. is referred to oxygen 16 alone regarded as a fixed constant. If referred to silver fixed at 107·876, the at. wt. of chlorine lies between 35·454 and 35·458, or 35·456 ± 0·0019; but if the value for chlorine is made to depend upon the cycle of relations between it and oxygen=16, "the at. wt. of chlorine lies between 35·453 and 35·459, or possibly 35·452 and 35·460;" or the at. wt. of chlorine is 35·456 ± 0·003, or possibly 35·456 ± 0·004. B. Brauner illustrates the idea geometrically by means of Fig. 22, which he says makes it much clearer than is possible by mathematical symbols, how the greater the distance right or left from the middle line corresponding with Ag=107·876, Cl=35·456, the smaller the probability that the corresponding value for the at. wt. will be correct. The international value for the at. wt. of chlorine is 35·46.

It is astonishing what a vast amount of labour has been expended in the struggle for increased accuracy in the determination of the at. wt. ratios. Some of the later determinations are masterpieces of precision. It is probable that the majority of these researches has been directed towards the chlorine : oxygen or the chlorine : hydrogen ratio on account of its fundamental importance. Even now J. F. W. Herschel's words [12] are not inapplicable :

> It is doubtful whether such accuracy in chemical analysis has yet been attained as to enable us to answer positively for a fraction not exceeding the three or four hundredth part of the whole quantity to be determined ; at least, the results of experiments obtained with the greatest care often differ by a greater amount.

Many have had misgivings as to the utilitarian value of the enormous labour which has been expended in this direction, and particularly when the best representative values of all the best results are usually rounded off to the nearest tenth when the at. wt. are employed in chemical calculations. Lord Kelvin's words are often quoted as a stimulus to greater and still greater precision :

> Accurate and minute measurement seems to the non-scientific imagination a less lofty and dignified work than looking for something new ; discoveries of science have been the reward of accurate measurement, and patient, long-continued labour in the minute sifting of numerical results.

The eighty or more individual numbers we call at. wt., adds T. W. Richards, "are perhaps the most striking of the physical records which Nature has given us concerning the earliest stages of the evolution of the universe. They are mute witnesses

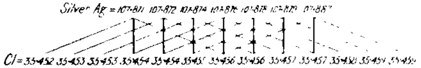

FIG. 22.—B. Brauner's Table of the Relation of the Atomic Weight of Chlorine to that of Silver (Oxygen 16).

of the first beginnings of the cosmos out of chaos, and their significance is one of the first concerns of the chemical philosopher."

We are now promised atoms of one element of different weight ; so that the observed at. wt. is a kind of average. If the atoms of different weight could be separated, the fractions would occupy the same position on the periodic table, and be chemically identical—they are called *isotopes*, and the subject is discussed in Vol. III. According to the positive ray spectrograph, F. W. Aston [13] obtained results which show that chlorine contains two isotopes of at. wt. 35 and 37 ; and W. D. Harkins has claimed that in the atomysis of hydrogen chloride the density of the fraction which remains in the diffusion tube increases at a rate corresponding with the assumption that the **chlorine isotopes** have at. wts. 35 and 37—with possibly a third of at. wt. 39. F. W. Aston added :

> At first sight it may seem incredible that chlorine, whose chemical combining weight has been determined more often and with greater accuracy than almost any other element, should not have given evidence of its isotopic nature in the past ; but it must be remembered that, in all probability, every one of these determinations has been performed with chlorine originally derived from the sea in which the isotopes, if ever separate, must have been perfectly mixed from the most remote ages. Chlorine from some other source, if such can be found, may well give a different result, as did radio-lead when examined.

The atomic weight of bromine.—The at. wt. of bromine has been determined by methods which follow in principle those employed for chlorine. A. J. Balard (1826),[14] the discoverer of bromine, transformed a known weight of potassium bromide into the sulphate, and also reduced silver bromide to metallic silver by means of zinc ; the numbers 74·7 and 75·3 were respectively obtained. J. von Liebig (1826)

also transformed potassium bromide into silver bromide, and obtained 75·2 for the at. wt of the element; C. Löwig (1829) obtained 75·76. These numbers are very low; this is, no doubt, due to the impurities present in the salts. J. J. Berzelius (1828) converted silver bromide into the chloride by the action of chlorine gas, and obtained a value *très approchée du but*, namely, 79·36. J. B. A. Dumas (1859), by the same method, obtained 79·95. W. Wallace precipitated silver bromide from arsenic tribromide, $AsBr_3$, by the addition of silver nitrate, and obtained an at. wt. of 79·738, when the at. wt. of silver is 107·97, and arsenic 75. The preceding determinations are usually disregarded in modern estimates of the at. wt. of bromine because of the then imperfect state of the art of chemical analysis as involved in the work.

J. C. G. de Marignac [15] decomposed potassium bromate by careful calcination, and precipitated the bromine from the resulting potassium bromide by treatment with silver nitrate. J. S. Stas reduced silver bromate by treatment with sulphurous acid; the ratio of silver to bromine was also determined by J. C. G. de Marignac and by J. S. Stas either by synthesizing silver bromide from its elements; or by converting potassium bromide into silver bromide. J. S. Stas' value, 79·9628 ±0·0032, has been recalculated by F. W. Clarke and by J. D. van der Plaats, who obtained respectively 79·951 and 79·955. A. Scott obtained values varying from 79·899 to 79·911 from his analysis of ammonium bromide. J. S. Goldbaum (1911) by the electrolytic method used for the ratio Na : Cl, obtained for the at. wt. of bromine 79·927, when the at. wt. of sodium is taken as 23·00. G. P. Baxter (1906) dissolved the purest silver in nitric acid, precipitated silver bromide by the addition of ammonium bromide, and finally fused the washed and dried product in bromine vapour. He obtained values ranging from 79·914 to 79·918—average 79·915—as the best representative value of his determinations. By collecting together all the direct and incidental determinations of the silver-bromine ratios since about 1843, F. W. Clarke obtained 79·9197 as the best representative value for the at. wt. of bromine (silver=107·880, oxygen=16); B. Brauner obtained 79·916, if silver be 107·880; 79·913, if silver be 107·876; and 79·909, if silver be 107·871; the error in the third decimal place is estimated to be about 0·004. P. A. Guye, E. Moles, C. K. Reiman, and W. J. Murray have computed the at. wt. of bromine from determinations of the density and compressibility of hydrogen bromide. The results lie between 79·924 and 79·926, when H=1·0076. The International table gives 79·92 as the best representative value when silver is 107·88.

The atomic weight of iodine.—In his historic *Mémoire sur l'iode* (1814), J. L. Gay Lussac [16] attempted to determine the at. wt. of iodine by the synthesis of zinc iodide, and in this manner he obtained the value 125 for the constant. H. Davy obtained 132 by converting sodium hydroxide into iodide. By an analogous process to that employed by J. L. Gay Lussac, W. Prout obtained 126. In 1825, T. Thomson obtained 124 as a result of decomposing potassium iodide. In 1828, J. J. Berzelius converted silver iodide into the chloride by the action of chlorine on the heated salt, and obtained values ranging between 126·26 and 126·39; and by the same method, J. B. A. Dumas obtained the value 126·59. In 1843, N. A. E. Millon determined the percentage of oxygen in potassium iodate and silver iodate and obtained respectively 126·697 and 125·33. The preceding determinations are usually disregarded in modern estimates of the at. wt. of iodine because "the art of qualitative analysis was then in its infancy."

J. C. G. de Marignac showed that the ignition of the iodate is not suited for the determination since some iodine is lost during the calcination, and he preferred the synthesis of silver iodide by dissolving a known weight of silver in nitric acid and precipitating the contained silver as iodide, by the addition of potassium iodide. The result furnished 126·537 and 126·550. J. S. Stas [17] analyzed silver iodate and determined both the water and the oxygen given off in each calcination, as well as the amount of silver iodide. He also reduced the iodate to iodide by sulphurous acid, and synthesized silver iodide by precipitation from silver nitrate by means of hydriodic acid, and by treating silver sulphate with ammonium iodide. The results varied

from 126·85 to 126·864—average 126·855. Both J. C. G. de Marignac's and J. S. Stas' results were affected by constant errors, the chief one being due to the occlusion of silver nitrate by the precipitated silver iodide. In 1902, A. Ladenburg claimed that the value 126·85 was about one-tenth too low; and soon afterwards, A. Scott obtained the value 126·912 as a result of two syntheses of silver iodide. P. Köthner and E. Aeuer synthesized silver iodide by heating the metal in iodine vapour, and by precipitation from silver nitrate by the addition of hydriodic acid, taking precautions to eliminate the occlusion of mother-liquor. As a result, they obtained 126·936 (oxygen 16).

A very careful series of determinations were made by G. P. Baxter about the same time. He precipitated silver iodide from silver nitrate by treatment of the soln. with ammonium iodide in the presence of an excess of ammonia; and also by converting iodine into ammonium iodide and precipitating the silver iodide by the addition of silver nitrate, taking precautions to avoid an excess of the latter reagent. As a result of the whole work, 126·929 was obtained for the at. wt. of iodine. G. P. Baxter and G. S. Tilley also measured the ratio of silver to iodine pentoxide, and found 0·646230, which makes the at. wt. of iodine 126·891. M. Guichard decomposed iodine pentoxide into oxygen and iodine by heat; the former was absorbed by red-hot copper, and the iodine condensed. He found that if oxygen has an at. wt. of 16, iodine is 126·915. G. Gallo electrolyzed a soln. of silver salt so that silver was deposited on the cathode, and the iodine liberated at the anode by titration with sodium thiosulphate. His determinations varied from 126·82 to 126·98—average 126·89.

Summing up the various determinations, F. W. Clarke obtained 126·920 ± 0·00033 as the best representative value for the at. wt. of iodine; and B. Brauner 126·932, if silver be 107·880; 126·927, if silver be 107·876; and 126·921, if silver be 107·871. It is very probable that the at. wt. is greater than 107·870 (oxygen 16) and smaller than 107·880, consequently, says B. Brauner, "the uncertainty in these values for the at. wt. of iodine does not extend to many units in the third decimal place." This makes the at. wt. of iodine 126·93 The International table gives 126·92 as the best representative value.

The anomaly in the at. wt. of iodine and tellurium with respect to their position in the periodic table has greatly stimulated researches on the at. wt. of these elements. It has been asked: Does iodine contain an undiscovered halogen element of higher atomic weight than iodine? In answer, G. P. Baxter converted iodine into hydriodic acid by hydrogen sulphide, and the hydriodic acid was converted back to iodine by distillation with potassium permanganate in small quantities at a time so as to obtain four fractions. No difference could be detected in the different fractions. If a halogen element were present in iodine with properties to be expected from the analogies with other members of the halogen family, it should have accumulated in the first fraction. Hence it is unlikely that iodine contains a halogen element of higher at. wt. than iodine. E Kohlweiler, however, claims to have evidence of the existence of **iodine isotopes.**

The molecular weights of iodine, bromine, and chlorine.—When the vapour density determinations of all known volatile chlorides are collected together, a table illustrated by the excerpt Table XI is obtained. The smallest combining weight of chlorine in any one of these compounds corresponds with the combining 35·46—oxygen=16—and accordingly this number is taken to represent the at. wt. of chlorine. The at. and eq. wt. of chlorine have the same numerical value. Similar results are obtained with the volatile fluorides, bromides, and iodides. The results show that the best representative values for the at. wt. of the halogens are Fl, 19·0; Cl, 35·46; Br, 79·92; and I, 126·92. The vapour densities of the halogens correspond with diatomic molecules; at elevated temp., as already shown, there are signs of dissociation into monatomic molecules, and this more particularly with iodine and bromine than with chlorine and fluorine. E. Paternó and R. Nasini[18] have determined the mol. wt. of bromine in aq. and acetic acid soln. by the f.p.

method, and the results correspond with the formula Br_2. Iodine in dil. benzene soln. corresponded with the molecule I_2, but in more conc. soln., the molecule seemed to be more complex. In acetic acid soln. the results were intermediate between those corresponding with mono- and di-atomic molecules. There has, however, been much discussion on the molecular condition of iodine in different solns.

TABLE XI.—MOLECULAR WEIGHTS OF VOLATILE COMPOUNDS.

Volatile chloride.	Vapour density.	Formula of compound : Mol. wt. = vapour density.	Amount of chlorine in the molecule.
Hydrogen chloride . . .	36·5	HCl	35·46
Chlorine . . .	70·9	Cl_2	70·92
Mercuric chloride . . .	273·6	$HgCl_2$	70·92
Arsenic trichloride . .	182·1	$AsCl_3$	106·38
Tin tetrachloride . . .	260·2	$SnCl_4$	141·84
Phosphorous pentachloride .	208·3	PCl_5	177·30

The valency of chlorine, bromine, and iodine.—Compounds are known in which the three halogens act as uni-, ter-, quinque-, or septa-valent elements. Usually, however, these elements are univalent. In chlorine dioxide, ClO_2, the chlorine is bi- or quadri-valent.[19] In M. Berthelot's hydrogen perchloride, HCl_3, the chlorine is probably tervalent, and R. Meldola (1888) showed that the oxygen in the hydrochloride of methyl oxide is best regarded as quadrivalent, the chlorine tervalent; thus, $(CH_3)_2 : O : Cl.H$. Iodine also appears to be tervalent in the so-called iodonium compounds.

When chlorine is passed into a chloroform soln. of iodobenzene, C_6H_5I, an addition compound phenyliododichloride, $C_6H_5I.Cl_2$, is produced in which the halogen atoms are probably tervalent. When this compound is treated with alkali hydroxide, *iodosobenzene*, C_6H_5IO, is formed; and when this compound is boiled with water, it produces *iodoxybenzene*, $C_6H_5IO_2$, and iodobenzene, C_6H_5I. By the action of silver hydroxide upon a mixture of eq. amounts of iodosobenzene, C_6H_5IO, and iodoxybenzene, $C_6H_5IO_2$, followed by treatment of the clear filtrate with potassium iodide, V. Meyer prepared the so-called **diphenyl iodonium hydroxide**, $(C_6H_5)_2 : I.OH$. The precipitated hydroxide forms an iodide, $(C_6H_5)_2 : I.I$, which crystallizes from alcohol in yellow needle-like crystals melting between 175° and 176°. The iodonium bases and salts resemble those of lead and silver but particularly those of thallium. The colour and solubility of the halides resemble the corresponding salts of these metals. The chloride is white, the bromide pale yellow, and the iodide yellow. The hydroxide and carbonate are soluble in water, and the soln. give an alkaline reaction, as is the case with the corresponding thallium salts. Diphenyl iodonium hydroxide gives a precipitate with ammonium sulphide, which looks like freshly precipitated antimony sulphide, and it consists mainly of a trisulphide—possibly $I-S-S-S-I=(C_6H_5)_2$. The nitrate, $(C_6H_5)_2I.NO_3$, acid sulphate, chromate, periodide, and other salts have been prepared. The base in question seems to be a derivative of an hypothetical **iodonium hydroxide**, $HO-I=H_2$, analogous with hydroxylamine, $HO-N=H_2$. **Monoiododiphenyliodonium** derivatives have been prepared by treating iodosobenzene, C_6H_5IO, with sulphuric acid at a low temp., and afterwards treating the dil. soln. with potassium iodide. The iodide, $(C_6H_5)I=I-C_6H_4-I$, and the other salts, as well as the base, $(C_6H_5)OH=I-C_6H_4-I$, resemble the corresponding salts of diphenyliodonium.

Compounds of the type KBr_3 are usually supposed to contain a tervalent halogen; the chlorates, bromates, and iodates, and compounds of the type CsI_5, to contain quinquevalent halogens; and the perchlorates and periodates and compounds of the type CsI_7, to contain septivalent halogens.

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§ 15. The Colour of Solutions of Iodine

The colours of iodine soln. may be roughly classed in two groups—violet and brown—but there are intermediate tints ranging from violet-red to reddish-brown. Thus, iodine gives a violet soln. with chloroform, and by the progressive addition of alcohol, the colour changes:

	Violet.	Reddish-violet.	Red.	Brown.
Alcohol	0·1	0·2	0·4	0·5 per cent.

According to A. Lachmann,[1] soln. with pure solvents are always either violet or brown, the intermediate tints are produced by impurities in the solvents. He adds that violet soln. are furnished by hydrocarbons, halogen compounds (not iodides), nitro-compounds, and carbon disulphide, while brown soln. are furnished by iodides, alcohols, ethers, ketones, acids, esters, nitriles, nitrilo-bases, and various sulphur compounds. There is a general tendency for the brown soln. to become violet when heated, and the violet soln. brown when sufficiently cooled.[2] For example, the violet soln. in paraffin oil becomes brown at $-90°$; and the brown soln. in the fatty esters becomes violet at 80°, while the soln. in ethyl ether remains brown up to the critical temp. of the solvent. H. Rigollot tried to establish a connection between the mol. wt. of the solvent and the colour of the soln. He found that for homologous compounds, and for derivatives of the same radicle, the absorption band is very slightly displaced towards the violet end of the spectrum. It is curious that what P. Walden called the multivalent solvents are those which produce brown soln., and, according to W. Vaubel, a similar remark applies to the solvents containing oxygen, sulphur, and nitrogen—*e.g.* ether, organic acids, esters, alcohols, aldehydes, and ketones. Dimethylpyrone produces brown soln., and it, according to A. W. Stewart and R. Wright, is an oxonium compound with quadrivalent oxygen. Similarly, the members of A. Lachmann's list of solvents which produce brown soln. have the characteristics of unsaturated compounds in that they form associated molecules, etc.

The absorption spectrum of the violet soln. is not very different from that of iodine vapour, although one is a band and the other a line spectrum. In his *Handbuch der Spectroscopie* (Leipzig, 1905), H. Kayser thus summarizes the observations on the absorption spectra of red and brown soln. of iodine:

> The red and brown soln. are quite transparent to the longer waves of light, and opaque to the shorter waves; the transition occurs in the visible spectrum for wave-lengths which are not very different. The violet soln. have a broad absorption band at about $500\mu\mu$, in consequence of which they have a stronger absorption in the red portion of the spectrum than red soln.; they begin in the blue, and again become quite transparent in the ultra-violet, where there is another absorption band whose position is not known very exactly, but which seems to be about $340\mu\mu$, and is probably extended to the limits of the spectrum.

The absorption spectrum of violet soln. is but little influenced by the nature of the solvent, by the temp. or by the concentration of the soln. With brown soln. of the same concentration, the absorption in the violet end of the visible spectrum and in the ultraviolet is much more marked. H. Gautier and G. Charpy, E. Wiedemann, and H. Ebert explain the peculiarities in the optical properties of iodine soln. by assuming a polymerization of the solute iodine which in the violet soln. contain I_2-molecules, and in the brown soln. I_{n+2}-molecules. Under any particular set of conditions, there is a state of equilibrium $I_{n+2} \rightleftharpoons nI_2$, which determines the tint of the soln. From measurements of the raising of the vap. press. of iodine in solvents which produce brown and violet soln., M. Loeb assumed that the iodine in the brown soln. is present as I_4 molecules and in the violet soln. as I_2 molecules. He explained the change from brown to violet with a rise of temp. by assuming that the equilibrium $I_4 \rightleftharpoons 2I_2$ is displaced in favour of the I_2 molecules, and conversely with a lowering of the temp.

E. Beckmann, however, has shown that the lowering of the f.p. of the violet and

brown soln. do not support M. Loeb's hypothesis.[3] For example, the mol. wt. of iodine at the f.p. of the following soln. is near to that theoretically required for I_2, namely 253·84.

Brown soln.		Violet or reddish-violet soln.	
Acetic acid	256	Carbon tetrachloride	252
Urethane	256	Chloroform	267
Ethyl acetate	245	Benzene	252
Methylal	253	Ethylene dibromide	244

Similarly with the raising of the b.p. in violet or reddish-violet soln. of iodine in benzophenone, carbon disulphide, ethyl chloride, chloroform, carbon tetrachloride, ethylene chloride or benzene; or in brown soln. of ethyl alcohol, methyl alcohol, thymol, ethyl ether, methylal, or acetone. The values for the last three solvents were rather low, presumably because of the chemical action of solute on solvent. High values with benzene are attributed to the formation of a solid soln. of solvent and solid. Confirmatory results were found by J. Hertz with naphthalene, and by E. Beckmann and P. Wäntig with pyridine. The results by I. von Ostromisslensky (*o*-nitrotoluene), by G. Krüss and E. Thiele (glacial acetic acid), and by H. Gautier and G. Charpy indicate polymerization, but they are not considered to be reliable.

In view of the fact that the mol. wt. of iodine in both brown and violet soln. is the same, E. Beckmann assumes that there is a partial combination of iodine with the solvent, S, forming a compound, say SI_2. Under any particular set of conditions there is a balanced reaction: $SI_2 \rightleftharpoons S + I_2$. With violet soln. the amount of combination is very much less than with brown soln. and the spectra approximate to that of iodine vapour. When the iodine soln. are heated the absorption band is displaced towards the red end of the spectrum approximating to that of iodine vapour; the converse obtains when the soln. are cooled. The displacement of the absorption bands with temp. is explained by assuming that the additive compound, SI_2, has a maximum absorption in the ultraviolet, and this is more or less affected by the absorption band due to free iodine. The spectra of some brown soln. become permanently altered on heating, showing that there is probably a considerable association between solvent and solute. Since the equilibrium is displaced in favour of an increase in the dissociation of the complex, SI_2, with a rise of temp., the heat of formation of the complex is probably positive. This agrees with the observed effect of temp. on the heat of soln. and solubility of iodine in different solvents. The negative heat of soln. for all solvents except pyridine is less for brown than for violet soln. P. Wäntig has isolated a compound of pyridine, Py, with iodine of the formula, PyI_2. D. McIntosh (1910) found that by cooling alcohol or acetone soln. of iodine to $-80°$ or $-90°$, iodine itself and not an addition product separates out, and he argues that the negative heat of soln. of iodine in most solvents rather lends itself to the assumption that the addition compound should dissociate with a falling temp. The observed negative heat of soln., however, is a difference between the exothermal heat of formation of the complex, SI_2, and the endothermal heat of soln.

In support of the theory that in brown soln. a complex of solute and solvent is formed, F. Dolezalek[4] having shown that the partial press. of each form of a substance in a soln. is proportional to the molecular proportion of it present in the mixture, P. Wäntig found that boiling soln. of iodine in ether, carbon disulphide, carbon tetrachloride, chloroform, and benzene agree with the assumption that even at the b.p. there is a considerable amount of association between iodine and the solvents which form brown soln. With this hypothesis also before them, J. H. Hildebrand and B. L. Glascock measured the depression of the f.p. of certain neutral solvents—bromoform and ethylene dibromide—produce by iodine and certain liquids separately and together. With mixtures which produce violet soln. the total depression of the mixture in the constituents are considered separately or together; with mixtures which produce brown soln. the total depression with the mixture is less than the sum of the separate depressions. This is taken as a proof

that in brown soln. the solvent and solute are more or less combined. H. M. Dawson compared the extrapolated value for the mol. vol. of iodine liquid at 18° with the mol. vol. in nitrobenzene (violet) soln. with its value in ethyl alcohol (brown) soln. Other solvents were used. The mol. vol. increases in the violet soln. and decreases in brown soln. This points to the formation of an addition compound of solvent and solute. C. Pomilio found that for the same concentration of iodine with red (benzene) and brown (alcohol, or ether) soln. the increase in the viscosity is greater than with violet soln., pointing to the formation of larger molecules in the brown soln. A. Hantzsch and A. Vagt, and M. Landau found that the partition coeff. of iodine between two solvents which form violet or brown soln. remains constant, but with two solvents which form violet and brown soln. respectively, the partition coeff. of iodine between the violet soln. is raised with decreasing concentration. This cannot be caused by a polymerization of the iodine in the violet soln., and it is assumed that it is due to an impoverishment of the solvent in the brown soln.; a rise of temp. diminishes the effect owing to the assumed dissociation of the addition compound. H. Gautier and G. Charpy[5] found that the chemical behaviour of brown soln. towards lead amalgam is different from violet ones in that brown soln. form yellow lead iodide before any green mercurous iodide is formed, while violet soln. form green mercurous iodide. It is said that brown soln. first form mercuric iodide which passes into soln.; this is reduced by the lead forming lead and mercurous iodides, the latter is reconverted into mercuric iodide, and so on until the lead is all converted into the yellow iodide. If no lead is present the mercuric iodide is reduced to the green mercurous salt by the excess of mercury. With violet soln. green mercurous iodide is supposed to be formed at once. Hence, "violet soln. of iodine contain the element in a more simple molecular condition with a tendency to form mercurous iodide at once." According to L. Carcano, violet soln. do not attack the skin so quickly as the brown ones.

According to A. Beer's law[6] the absorption of light in passing through a layer of fluid of unit thickness increases in geometrical series when the concentration increases in arithmetical series; and according to K. Vierordt's rule, the coeff. of absorption, a, is proportional to the concentration C of the soln. These rules are applicable provided the molecular state of the soln. is not altered by a change in the concentration—say by ionization, or degree of association of soln. or solvent. P. Wäntig found that neither rule is applicable to soln. of iodine, and it is assumed that the solute is partly ionized.

According to J. Amann,[7] brown soln. of iodine contain ultra-microscopic particles, while the violet soln. contain none. The violet-red soln. in benzene, toluene, and xylene are photosensitive in that clouds of ultramicroscopic particles are formed in white light, and the soln. rapidly turn brown. The soln. return to their original state in darkness. In some cases, iodine soln. are true soln. either of free iodine or of an addition compound; and in other cases they contain free colloidal iodine or of a polymerized addition compound. In some cases ultra-microscopic suspended particles of iodine are present.

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§ 16. Binary Compounds of the Halogens with One Another

Fluorine and chlorine form neither compounds nor mixed crystals, although there may be a eutectic. H. Moissan could detect no signs of a reaction when fluorine gas was led into an atm. of chlorine gas. The two liquids are miscible. Several fluochlorides are known. Fluorine, however, does unite vigorously with bromine and iodine, forming BrF_3 and IF_5 respectively. Chlorine and bromine form mixed crystals but no compound; bromine and iodine form mixed crystals and a compound IBr; while chlorine and iodine form two compounds—ICl and ICl_3—in which the iodine appears to function as a metal. Iodine thus combines with all the halogens; bromine does not combine with chlorine, but it combines with both iodine and fluorine; chlorine combines with iodine alone; and fluorine with both bromine and iodine, but not with chlorine. When the four halogens are taken in pairs in the order of their at. wt., the chemical affinity between fluorine and chlorine is least and that between bromine and iodine is greatest. The known binary inter-halogen compounds are:

	Fluorine.	Chlorine.	Bromine.
Chlorine	No action	—	Mixed crystals
Bromine	BrF_3	Mixed crystals	—
Iodine	IF_5	ICl; ICl_3	IBr

Fluorine and bromine.—While no sensible reaction between fluorine and chlorine has been observed, H. Moissan [1] found that fluorine unites violently with cold bromine vapour, and the reaction is attended by *une flamme éclairante*, but with the evolution of little heat. P. Lebeau found that no flame is produced if dry liquid bromine is employed, and he showed that the product of the reaction is **bromine trifluoride**, BF_3, a result almost simultaneously established by E. B. R. Prideaux. No reaction—solvent or chemical—occurs between liquid fluorine and solid bromine, and the fluorine can be distilled from the latter without any sign of interaction. There is no indication of the formation of a lower bromide, say, BrF; and attempts to prepare a higher fluoride, say BrF_4, by passing a large excess of fluorine over the trifluoride, were fruitless. Bromine trifluoride was also made by the action of fluorine on potassium bromide: $KBr+2F_2=KF+BrF_3$.

Bromine trifluoride is a colourless liquid with a smaller sp. gr. than bromine; it freezes to a crystalline mass melting at $-2°$ (E. B. R. Prideaux), or at 4° to 5° (P. Lebeau), and boils between 130° and 140°—the exact temp. was not determined because the vapour attacked the thermometer. The liquid fumes strongly in air, and acquires an orange-yellow colour. The vapour is very irritating and corrosive. The reactivity of the trifluoride recalls that of fluorine itself. It reacts violently with water, giving off oxygen, and forming a mixture of hypobromous, hydrofluoric, and bromic acids; and an analogous reaction occurs with soln. of the alkali carbonates. These reactions are taken as evidence that bromine is the electropositive and fluorine the electronegative component in the compound. Even at $-10°$ the solid trifluoride reacts incandescently with iodine to form iodine pentafluoride, IF_5, similarly with bromine; with sulphur, to form sulphur bromide; and with red phosphorus, arsenic, antimony, boron, and silicon. It reacts with warm

carbon ; and attacks most metals and their compounds. It behaves like fluorine towards organic compounds.

In 1844, H. B. Leeson[2] claimed to have made a bromine fluoride by leading fluorine into bromine, but fluorine was not unequivocally isolated until 1886, and therefore this claim does not hold good ; some other products must have been formed. The same remark applies to M. Aubrée, M. Millet, and M. Leborgne's claim to the use of bromine chloride in photographic work.

Fluorine and iodine.—According to H. Moissan,[3] when a current of fluorine is directed on to a fragment of dry iodine, the iodine burns with a pale flame ; there is a large evolution of heat. Iodine liquefies almost immediately the fluorine begins its attack, forming a homogeneous dark liquid which on further action forms an upper colourless and a lower dark layer. Under suitable conditions, the product of the action can be condensed to a dense colourless, fuming liquid which resembles the **iodine pentafluoride,** first prepared by G. Gore in 1875 by the action of iodine on silver fluoride in a platinum vessel: $5AgF+3I_2 \rightarrow IF_5+5AgI$. The same compound is formed by the action of fluorine on hydrogen iodide : $HI+3F_2 \rightarrow IF_5+HF$. Liquid fluorine exerts no chemical or solvent action on iodine, and the liquid can be distilled from the solid without any sensible change. If a tube of liquid fluorine and iodine be sealed off, and removed from the cooling agent, the layer of fluorine near the iodine acquires a dark colour, the iodine liquefies, an energetic action sets in, and white fumes are projected some way up the tube, and finally a pale green flame appears for a few seconds. An analysis of the liquid by E. B. R. Prideaux corresponded with the formula IF_5. Fruitless attempts were made to prepare a higher fluoride.

The sp. gr. of the liquid pentafluoride approximates to 3·5 ; it boils at 97° without decomposition, but it dissociates between 400° and 500° ; the liquid freezes at −8° to a white solid with a smell resembling that of camphor ; the fumes from the liquid affect the respiratory organs. The liquid dissolves iodine and bromine forming brown-coloured soln. Iodine pentafluoride is very reactive although it is the most stable of the halogen fluorides. It reacts with water with *le bruissement* of red-hot iron forming iodic and hydrofluoric acids : $2IF_5+5H_2O=I_2O_5+10HF$. An analogous reaction occurs with alkaline soln., when the alkali iodate and fluoride are formed. The liquid can be distilled in hydrogen without chemical change ; oxygen has no action at 100° ; chlorine reacts in the cold, forming iodine chloride ; bromine produces bromine trifluoride, and iodine bromide, IBr ; phosphorus reacts vigorously, forming phosphorus pentafluoride, PF_5, and iodine ; arsenic and antimony act like phosphorus ; with sulphur it forms sulphur hexafluoride, SF_6, and free iodine ; carbon reacts energetically forming carbon tetrafluoride, CF_4, and iodine ; crystalline silicon is not attacked in the cold, but on warming, the reaction resembles that with carbon ; boron acts similarly. The alkali metals at first react energetically with the liquid, but the reaction soon comes to a standstill owing to the formation of a protective layer of iodide and fluoride ; the molten metals react with explosive violence. Silver, mercury, iron, and magnesium are not attacked at 100°, platinum is attacked at a red heat. Silica is attacked slowly in the cold, rapidly when heated ; dry glass is attacked with but little vigour ; and the silicon alloys—*e.g.* ferrosilicon —are rapidly attacked when warmed. Potassium hydride, KH, reacts energetically producing a violet vapour of iodine and hydrogen iodide, and solid potassium iodide and fluoride. Calcium carbide does not react at ordinary temp., but it does so when warmed. Calcium carbonate and phosphate do not react with the pentafluoride. The liquid sinks in conc. sulphuric acid and is slowly decomposed ; it mixes in all proportions with nitric acid and is likewise slowly decomposed—hydrofluoric acid is formed in both cases. It reacts vigorously with hydrochloric acid. Carbon disulphide dissolves the liquid forming a dark violet soln. ; turpentine is energetically decomposed ; benzene at first dissolves the liquid, but a vigorous reaction soon starts.

Chlorine and bromine.—In 1826 A. J. Balard[4] believed that he had formed a

compound of these two elements as a strongly refracting yellowish-red liquid, by passing chlorine into bromine, and condensing the vapour in a freezing mixture. C. Löwig and C. F. Schönbein (1863) confirmed these observations, and the former also claimed to have made a chlorobromine hydrate, $BrCl.5H_2O$. W. Bornemann (1877) further investigated the subject, and said that the chlorobromine is formed only at temp. below 0°, and that the alleged hydrate is probably a mixture of the hydrates of chlorine and bromine. According to J. Krutwig, chlorine acts on silver bromate, $AgBrO_3$, at 50° forming silver chloride, oxygen, and chlorine monobromide. F. Donny and J. Mareska (1845) believed that the two elements united chemically at −90°; and V. Thomas and P. Dupois (1906) not only claimed that *bromine monochloride*, BrCl, is formed by the action of liquid chlorine on bromine, but they state that *bromine trichloride*, $BrCl_3$, is formed as a red solid by the action of liquid chlorine on bromine monochloride. L. W. Andrews and H. A. Carlton (1907) determined the sp. gr. of mixtures of liquid chlorine and bromine, and concluded that because there is a small contraction "chemical combination probably occurs to a limited extent between these two elements."

In 1882, M. Berthelot expressed doubts about the alleged formation of compounds of these two halogens because of the small heat developed during their supposed union: $Br_{liq.}+Cl_{liq.}=BrCl_{liq.}+0.7$ cal. The work of P. Lebeau (1906) [5] and B. J. Karsten (1907) has shown that M. Berthelot's suspicion was well-founded.

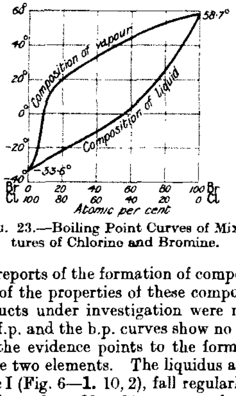

FIG. 23.—Boiling Point Curves of Mixtures of Chlorine and Bromine.

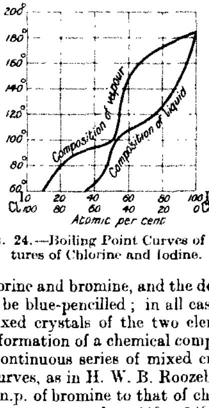

FIG. 24.—Boiling Point Curves of Mixtures of Chlorine and Iodine.

The reports of the formation of compounds of chlorine and bromine, and the description of the properties of these compounds are to be blue-pencilled; in all cases the products under investigation were no doubt mixed crystals of the two elements. The f.p. and the b.p. curves show no signs of the formation of a chemical compound, but the evidence points to the formation of a continuous series of mixed crystals of the two elements. The liquidus and solidus curves, as in H. W. B. Roozeboom's Type I (Fig. 6—**1.** 10, 2), fall regularly from the m.p. of bromine to that of chlorine, and from about 20 to 90 per cent. of chlorine the two curves are from 10° to 14° apart, being respectively convex and concave to the horizontal axis; but there is no sign of a maximum. The results show that the composition of the crystals is dependent on the temp. The fact that analyses of the supposed compound furnished numbers in agreement with BrCl was a consequence of the solubility of chlorine in bromine. Fig. 23 shows the composition of the vapour and that of the liquid with which it is in equilibrium at the b.p. with mixtures containing varying proportions of the two elements. There is no sign of an approximation of the two curves at intermediate points such as would occur if chemical combination occurred, and such as actually occurs with the corresponding curves for chlorine and iodine, Fig. 24, where the curves approach, and almost touch one another at a point where the two components are present in equi-atomic proportions, ICl. In the latter case, therefore, it is inferred that the compound ICl exists in the vapour phase, and is only slightly

dissociated at 100°, the b.p. of the particular mixture in question. While the evidence from physical chemistry thus gives no support to the existence of a bromine chloride, M. Delépine and L. Ville believe that such a compound does exist because a soln. of chlorine in bromine reacts with ethylene forming chlorobromoethane.

Chlorine and iodine.—In the course of his historic research on iodine, J. L. Gay Lussac (1814)[6] prepared a compound of iodine and chlorine by the action of chlorine gas on iodine—the gas was absorbed by the solid forming a reddish-brown liquid which is so remarkably like bromine, that before that element had been recognized as a distinct chemical individual by A. J. Balard, J. von Liebig mistook bromine for iodine chloride. If the chlorine be in excess, citron-yellow needle-like crystals are formed. The liquid product is iodine monochloride; the crystalline solid is iodine trichloride. H. Davy called the product formed by the action of iodine on chlorine, *chlorionic acid*, and he regarded it as a compound consisting of "one proportion of iodine and one of chlorine"—*i.e.* iodine monochloride.

W. Stortenbeker's[7] investigation on the f.p. curve, Fig. 25, left no doubt as to the existence of these two iodine chlorides. The f.p. curve shows two maxima, one at 27·2° corresponding with the so-called **iodine α-monochloride**, and the other at 101° corresponding with iodine trichloride; the corresponding eutectics are at 7·9° and 22·7°. In 1854, J. Trapp showed that there are two modifications of the monochloride which W. Stortenbeker respectively distinguished as the α- and β-forms. The α-modification is formed if the fused mass is rapidly cooled when it forms ruby-red, transparent, needle-like crystals belonging to the cubic system. The sp. gr. is 3·18223 (0°) and 3·12988 (18°) according to T. E. Thorpe. The **iodine β-monochloride** is formed when the undercooled liquid is slowly cooled by a freezing mixture to −10°. The crystals are brownish-red, six-sided rhombic plates resembling solid iodine; they melt at 13·9° or more exactly 13·92°. The α-form is the stable variety. Both forms when melted furnish the same liquid; and the m.p. of each variety is lowered if either iodine or chlorine be in excess as indicated in the diagram. The β-crystals are more stable in the presence of an excess of iodine, and less stable in the presence of an excess of chlorine. The existence of iodine monochloride in freezing soln. has also been established by the experimental results graphed in Fig. 25.

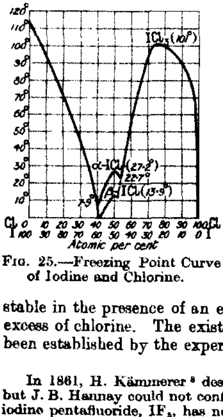

FIG. 25.—Freezing Point Curve of Iodine and Chlorine.

In 1861, H. Kämmerer[8] described what he considered to be *iodine tetrachloride*, ICl_4, but J. B. Hannay could not confirm the report. *Iodine pentachloride*, ICl_5, analogous with iodine pentafluoride, IF_5, has not been isolated. This compound may be formed by the action of liquid chlorine on iodine; if so, it is so unstable at ordinary press. that it has not been recognized.

The preparation of iodine monochloride.—Iodine monochloride can be made by passing dry chlorine over dry iodine confined in a retort until the solid has completely liquefied; or, as recommended by W. Bornemann,[9] until crystals of iodine trichloride appear. The liquid is then distilled; a reddish-brown fluid is obtained which, according to P. Schützenberger, should be rectified by distillation a couple of times between 100° and 102°. The analysis approximates to iodine monochloride, ICl. A. Bunsen (1852) obtained the same compound by boiling iodine with an excess of aqua regia, diluting the liquid with water, extracting with ether, and evaporating off the ether.

To prepare iodine monochloride, mix 100 grms. of finely powdered iodine with 300 c.c. of hydrochloric acid (sp. gr. 1·15) in a porcelain basin; and add 28 c.c. of nitric acid (sp. gr.

1·41) to provide sufficient chlorine to convert all the iodine into its chloride. The mixture is continuously stirred on a water bath at about 40°, the colour changes from brown to pale-yellow when the reaction begins; the iodine then dissolves and the soln. becomes orange-coloured—no chlorine escapes under these conditions. The water in the bath is then boiled to expel the nitrosyl chloride. With the excess of hydrochloric acid used, the soln. of iodine chloride is stable and does not decompose on boiling.

G. S. Sérullas recommended passing chlorine through tincture of iodine, but there is then a complication due to the action of the gas on the alcohol. Iodine monochloride is formed by the action of hypochlorous acid or of sulphuryl chloride, SO_2Cl_2, on iodine (O. Ruff), or, according to A. Töhl, on iodobenzene, *p*-iodotoluene, and analogous aromatic iodides—a trace of water may be required to start the reaction. These reactions are not recommended as processes for preparing the compound. According to O. Ruff, the sulphuryl chloride does not act on iodine alone, but in the presence of aluminium chloride or iodide, iodine monochloride is formed if the sulphuryl chloride be not in excess: $SO_2Cl_2+I_2=2ICl+SO_2$; if the sulphuryl chloride be in excess, some iodine trichloride is also formed. According to R. Bunsen, nitrogen iodide dissolves in hydrochloric acid without developing a gas, and the liquid contains iodine monochloride.

In general, A. Skrabel and F. Buchta[10] have shown that iodine monochloride is alone produced when iodine or an iodide is treated with a strong oxidizing agent—iodic acid, chloric acid, chlorine, hypochlorites, permanganates, etc.—in the presence of conc. hydrochloric acid. It is supposed that hypoiodous acid, I.OH, is first formed, and subsequently transformed to iodine monochloride by the acid. Thus, C. Roberts recommended reducing iodic acid by potassium iodide in the presence of conc. hydrochloric acid. Hydrogen chloride also reduces iodine pentoxide with the formation of iodine monochloride. J. J. Berzelius' process is one of the most convenient modes of preparing iodine monochloride, namely, by heating an intimate mixture of iodine and potassium chlorate; P. Schützenberger recommended four parts by weight of chlorate to one of iodine. The reaction is symbolized: $2KClO_3+I_2=2KIO_3+Cl_2$. The chlorine so formed unites with the excess of iodine to form the monochloride. According to T. E. Thorpe and G. H. Perry, potassium chloride, potassium perchlorate, and iodine pentoxide are formed only when the mixture is heated to too high a temp. T. E. Thorpe recommends purifying the product by distilling it from powdered potassium chlorate.

The properties of iodine monochloride.—As just indicated the hyacinth-red or ruby-red solid exists in two forms; as indicated above, W. Stortenbeker[11] found that the α-variety has a m.p. of 27·2° or 27·165° (G. Oddo), and the β-variety, 13·9° or 13·92° (G. Oddo). The older determinations by J. Trapp, J. B. Hannay, and P. Schützenberger are inaccurate on account of the use of impure specimens. The b.p. of the molten iodine monochloride has not been yet determined very precisely. Determinations by T. E. Thorpe, G. Oddo and E. Serra, and J. B. Hannay varied from 100° to 102°; W. Stortenbeker interpolates from his vap. press. measurements 94·7°, and B. J. Karsten finds 97·4°. Possibly the higher boiling product contains some iodine in soln. owing to the decomposition: $3ICl\rightarrow I_2+ICl_3$, observed by R. Kane and W. Bornemann, and the sublimation of the trichloride, which leaves the molten liquid richer in iodine. The dissociation of the molten monochloride can be but small since W. Stortenbeker found at 30°, 51·1, and at 80°, 52·1 atomic per cent. of chlorine; even at the b.p., the dissociation is but small, as is evident from B. J. Karsten's diagram, Fig. 25. As the composition of the liquid phase deviates from the proportion Cl : I=1 : 1, so does chlorine tend to accumulate in the vapour phase, and only when the composition ICl is approached do both phases have the same composition. The lower end of the boiling curve corresponds with the separation of ICl_3 from the molten liquid. The vap. press. of iodine monochloride at its m.p. 27·2° is 39 mm. The brownish-red colour of the vapour indicates that iodine monochloride is stable; the absorption spectrum of a 30 c.m. layer of vapour at 40°, and 30 mm. press., was found by D. Gernez to be different from that of

chlorine and that of bromine, chiefly in virtue of its possessing fine lines in the green. H. E. Roscoe and T. E. Thorpe drew attention to the resemblance of the spectrum of iodine monochloride to that of bromine.

W. Stortenbeker found the heat of the transformation to be $ICl_\beta \rightarrow ICl_\alpha + 203$ cals., or, according to S. Tanatar, 273 cals. The heat of fusion of the α-form is −16·42 cals. per gram or −2658 cals. (−2320 cals. according to S. Tanatar) per mol.; and for the β-form, −14 cals. per grm., or −2267 cals. per mol. W. Stortenbeker also found the sp. ht. of the α-form to be 0·083 between −13·5° and 15°; for the β form, 0·085 between −10° and 0°; and 0·158 for the liquid between 15° and 77°. K. Strecker found the ratio of the two sp. ht. to be $\gamma=1·317$; and $C_p=0·0512$; $C_v=0·0389$. The sp. ht. of both the α- and β-forms are nearly alike, and hence the heat of transformation is nearly independent of temp. The heat of formation, according to J. Thomsen, $I_{solid}+Cl_{gas}=ICl_{liquid}+5·8$ Cals., and according to B. Berthelot, for $I_{solid}+Cl_{gas}=ICl_{solid}+6·8$ cals. No difference can be detected in the nature of the brownish-red oily liquid, iodine monochloride, derived from the α- and β-solids. S. Tanatar found the sp. gr., and K. Beck the viscosities, to be the same, and the heat of resolidification to the α-form are the same. Iodine monochloride is miscible with iodine or bromine in all proportions. The sp. gr. of the α-solid is 3·18223 at 0°, 3·1288 at 17·93°—J. B. Hannay's values are a little higher; the sp. gr. of the liquid is:

	16°	30°	45°	60°	72°	86°	95°	101·8°
Sp. gr. . . .	3·2856	3·180	3·132	3·084	3·032	2·988	2·964	2·882

T. E. Thorpe's formula for the specific volume v at the temp. θ is $v=1+0·0009158960\theta+0·00000083296\theta^2+0·0000000027500\theta^3$. The vapour density is that theoretically required for ICl; with oxygen 32, the value for ICl is 162·38; at 120°, the vapour density is 160·6, and at 512°, 156·4. Conclusions as to the degree of dissociation at different temp. cannot be derived from the vapour density determinations since it proceeds without changing the number of molecules—$2ICl \rightarrow I_2+Cl_2$. Iodine trichloride vapour is almost completely dissociated into the monochloride and chlorine. K. Beck's value for the viscosity is 7·029 at 15°, 5·069 at 28·4°—benzene at 5° unity.

Unlike iodine, the monochloride does not blue starch, but it bleaches indigo and litmus soln. The aq. soln. can dissolve much iodine. Iodine monochloride dissolves in carbon tetrachloride and in liquid sulphur dioxide, forming red soln.; arsenic trichloride forms a reddish-brown soln. The mol. wt.[12] of the α-form of iodine monochloride in phosphoryl chloride determined by the cryoscopic method, corresponds with the formula ICl. The b.p. of carbon tetrachloride is lowered by iodine trichloride owing to the fact that the solute sublimes between 70° and 75°. The b.p. of carbon tetrachloride is also lowered by iodine monochloride; G. Oddo and E. Serra attribute this to dissociation in accord with the equation $9ICl \rightarrow I_2+I_4+3ICl_3$, and the effect of the trichloride in lowering the b.p. masks the rise due to the iodine. The depression of the f.p. of glacial acetic acid by iodine monochloride is normal, corresponding with the formula ICl.

Iodine monochloride is stable in hydrochloric acid in which it forms a yellow soln., but in water [13] it is presumably hydrolyzed forming hypoiodous and hydrochloric acids: $ICl+H_2O=HOI+HCl$, corresponding with the fact that the iodine is more electropositive than chlorine. The hypoiodous acid immediately breaks up into iodic acid, HIO_3, and iodine: $5HIO=2H_2O+2I_2+HIO_3$. The joint effect of these two consecutive reactions is symbolized: $5ICl+3H_2O=2I_2+5HCl+HIO_3$, an equation which is virtually that employed by J. L. Gay Lussac in 1814 to represent the formation of iodine and iodic acid when iodine monochloride is decomposed by water. According to W. Bornemann, the iodine which separates is brought into soln. by treatment with hydrochloric acid. The iodine monochloride forms a complex, ICl.HCl, in the presence of hydrochloric acid. P. Schützenberger found that this compound may be isolated by extracting the soln. with ether. As the acid is diluted, the compound is progressively hydrolyzed. Aq. soln. of the alkali

hydroxides behave in a somewhat similar manner to water furnishing the alkali chloride and iodate, and free iodine; the latter may react with the excess of alkali lye forming a mixture of iodide and iodate. If the alkali be not in excess, H. Grüneberg found some alkali chlorate is formed. According to K. J. P. Orton and W. L. Blackman, an alkali hypoiodite can be detected for a short time in the soln. obtained by treating iodine monochloride with a soln. of an alkali carbonate, or lime—or baryta-water. With ammonia, A. Mitscherlich and R. Bunsen found that ammonium chloride and nitrogen iodide are formed.

The salts of the oxychlorine acids are decomposed by iodine monochloride, forming iodates and free chlorine; thus at ordinary temp. the hypochlorites are rapidly decomposed: $3KOCl+ICl \rightarrow KIO_3+2KCl+Cl_2$, and the chlorates slowly: $KClO_3+ICl \rightarrow KIO_3+Cl_2$. Consequently, both iodine, and iodine as the monochloride, displace the chlorine from the oxychlorine acids. The reverse is the case with the halide salts. Iodine monochloride behaves towards mercury, aluminium, phosphorus, arsenic, antimony, bismuth, tin, etc., very much like free chlorine forming the metal chloride, some iodide, and free iodine. Aluminium foil is not attacked very much at first, but it afterwards burns with a bluish-white flame. Copper foil acts very slowly, but the powdered metal reacts quickly. Potassium explodes in contact with iodine monochloride, but the action with sodium is very slow. Sulphur reacts slowly forming free iodine and sulphur chloride, selenium acts more quickly, and tellurium more quickly still. Hydrogen sulphide and sulphur dioxide are decomposed with the separation of iodine, and iodine reacts with the excess of sulphur dioxide [14] A sat. soln. in carbon disulphide gives off white fumes, and on the addition of water, an oily mixture of carbon disulphide, carbon tetrachloride, sulphur chloride, and carbon thiochloride is precipitated. Metal oxides—*e.g.* lead dioxide, cupric oxide, mercuric oxide, etc.—form metal chlorides and iodides, free iodine, and oxygen. With galena, iodine monochloride forms lead iodide and sulphur chloride. Mercuric chloride precipitates mercuric iodide from conc. soln. of iodine monochloride and iodine trichloride remains in soln. A little stannous chloride, $SnCl_2$, precipitates iodine and forms stannic chloride, $SnCl_4$, but with more stannous chloride, stannous iodide, SnI_2, is formed.

M. Faraday [15] found that liquid iodine chloride can be electrolyzed, the iodine collecting at the cathode, the chlorine at the anode. According to the ionic hypothesis, this means that iodine chloride is partially ionized, $ICl \rightleftharpoons I^{\cdot}+Cl'$, that is, iodine monochloride is a compound of the cation, $I^{\cdot}$, with the anion, Cl'. This also corresponds with the chemical behaviour of this compound, and with O. Walden's experiments on the electrical conductivity of soln. of iodine monochloride in inorganic solvents—liquid sulphur dioxide, arsenic trichloride, and sulphuryl chloride. L. W. Andrews [16] assumed that iodine monochloride is the chlorine derivative of hypoiodous acid, HOI; A. Skrabel and F. Buchta consider it best to regard the hydroxyl derivative HO.I as a base. Iodine monochloride forms an addition compound with hydrogen chloride, ICl.HCl, as found by P. Schützenberger,[17] in which the stability appears to be greatly increased. P. Schützenberger's compound may be regarded as a complex acid, $HICl_2$, with the ions H' and ICl_2'; and the polyhaloids of H. L. Wells and S. L. Penfield, and A. Geuther as salts of this acid—*e.g.* the compound KCl.ICl becomes $KICl_2$; $N(CH_3)_4Cl.ICl$ becomes $N(CH_3)_4.ICl_2$; etc. Phosphorus pentachloride with iodine monochloride forms phosphorus trichloride and the compound PCl_2I.

Iodine trichloride.—This compound was discovered by J. L. Gay Lussac as the result of treating warm iodine or iodine monochloride with an excess of chlorine. The trichloride collects as a citron-yellow crystalline sublimate on the cooler parts of the vessel. It is also formed by the action of liquid chlorine on iodine, or an iodide—say lead iodide.[18] The iodine trichloride is almost insoluble in liquid chlorine, and hence, say V. Thomas and P. Dupuis, this method of preparation is very convenient. It is also formed by the action of dry chlorine on hydrogen iodide (A. Christomanos); silver iodate (J. Krutwig); or methyl iodide (L. von

Ilosvay); by the action of hydrogen chloride on iodic acid (G. S. Sérullas); of phosphorus pentachloride on iodine pentoxide (O. Brenkn); of iodine on sulphuryl chloride in excess (O. Ruff): $3SO_2Cl_2+I_2=2ICl_3+3SO_2$; and by heating iodine monochloride.

To prepare iodine trichloride, heat 20 grms. of iodine in a retort, *A*, Fig. 26, which delivers into a glass balloon *B* filled with chlorine, and connected with a Kipp's apparatus *C* delivering chlorine. The chlorine is rapidly absorbed as soon as it comes in contact with the vapour of iodine, and reddish-yellow crystals of iodine trichloride are formed on the walls of the balloon. The excess of chlorine is finally expelled by a stream of carbon dioxide. If the crystals are desired, the balloon must be broken; if a soln. of iodine trichloride is desired, the crystals can be dissolved in about ten times their weight of water.

Iodine trichloride forms long citron-yellow needles, and also large reddish-brown rhombic plates. The sp. gr. at 15° is 3·117 (A. Christomanos). This compound melts in a sealed tube under the press. of its own vapour at 101° and 16 atm. press. forming a reddish-brown liquid which freezes to crystals of the same colour. The citron-yellow crystals are obtained by sublimation. The differences in colour and appearance led W. Stortenbeker to say that the trichloride is dimorphous. The crystals readily decompose in air, but they can be preserved unchanged in an atm. of chlorine, and A. Christomanos states that the compound is so volatile that it sublimes at −12° in an atm. of carbon monoxide or dioxide, and at 0° in an atm. of oxygen. According to P. G. Melikoff, the vapour of iodine trichloride is almost completely dissociated into the monochloride and free chlorine at about 77° and atm. press. The f.p. curve is indicated in Fig. 25, and the b.p. curve in Fig. 24. The heat of formation $I_{solid}+3Cl_{gas}=ICl_{3solid}+21·49$ Cals. (J. Thomsen), or +16·3 Cals. (M. Berthelot); or $ICl_{solid}+2Cl_{gas}=ICl_{solid}+15·66$ Cals. (J. Thomsen), or +9·5 Cals. (M. Berthelot).[19]

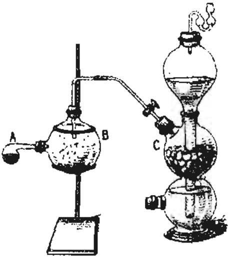

FIG. 26.—The Preparation of Iodine Trichloride.

At ordinary temp. hydrogen has no action on iodine trichloride, but when warmed, it forms the monochloride and hydrogen chloride: $H_2+ICl_3=ICl+2HCl$; and at a still higher temp., hydrogen iodide and chloride are formed. The trichloride behaves towards potassium, phosphorus, and the oxychlorine acids in an analogous manner to the monochloride. According to H. Basset and E. Fielding, chlorine monoxide—gaseous or dissolved in carbon tetrachloride—furnishes iodine pentoxide and free chlorine: $2ICl_3+5Cl_2O=I_2O_5+8Cl_2$; it does not act on iodic acid or on iodine pentoxide. Iodine trichloride dissolves in benzene, carbon tetrachloride, nitrobenzene, liquid sulphur dioxide, etc., and the two last-named soln. conduct electricity.[20] Iodine trichloride dissolves in alcohol and ether, but slowly decomposes these liquids; and with carbon disulphide, said J. B. Hannay, it reacts: $4CS_2+6ICl_3=2CCl_4+2CSCl_2+3S_2Cl_2+3I_2$.

The trichloride is less soluble in water than the monochloride, and it forms a dark yellow, strongly acid liquid which fumes slightly in air. Water furnishes similar products to those obtained with the monochloride. According to A. Skrabel and F. Buchta, the first action of water is to hydrolyze the compound: $ICl_3+H_2O\rightleftharpoons HCl+OCl_2OH$. It is more generally supposed that the first action of water is to hydrolyze the trichloride: $ICl_3+3H_2O\rightleftharpoons H_3IO_3+3HCl$; the iodic acid, H_3IO_3, immediately breaks down into iodic and hypoiodous acids: $2H_3IO_3=HOI+HIO_3+2H_2O$, and the hypoiodous acid reacts with the hydrochloric acid formed in the first stage of the reaction: $HOI+HCl=ICl+H_2O$. According to P. Schützenberger, the reaction progresses: $2ICl_3+3H_2O=5HCl+ICl+HIO_3$, and the hydrolysis is

complete if 10 to 20 mols. of water are used for each mols. of the trichloride; if less water is used, some trichloride remains in soln. undecomposed. In consequence of the hydrolysis, the aq. soln. is stable only in the presence of much hydrochloric acid—possibly a complex $ICl_3.HCl$ is likewise formed. The action of soln. of alkali hydroxides follows similar lines—chlorides, chlorates, iodides, iodates, and free iodine are formed as with the monochloride. If the alkali be not in excess, the reaction is represented: $5ICl_3+18KOH\rightarrow3KIO_3+I_2+15KCl+9H_2O$. There are some side reactions furnishing hypochlorites and chlorates, and, according to J. Philipp, perchlorates, corresponding with the tendency of the trichloride to lose free chlorine: $ICl_3=ICl+Cl_2$. In alcoholic solution, potassium hydroxide forms with the trichloride, potassium iodide, iodate, chloride, and iodoform. According to A. Christomanos, ammonia in excess forms nitrogen iodide, and ammonium iodide and chloride. Sulphuric acid precipitates from aq. or hydrochloric acid soln. of the trichloride a white precipitate which soon changes to a yellow colour, and which has some analogies with P. Chrétien's iodosulphate,[21] $I_2O_3.SO_3.\frac{1}{2}H_2O$; it dissolves when the mixture is heated but separates out on cooling; nitric acid precipitates iodine with the evolution of chlorine.

Silver foil is transformed by an aq. soln. of the trichloride into silver chloride and iodide; silver oxide with an excess of the trichloride is transformed into the chloride and iodic acid; with more silver oxide, silver iodate is formed; and with an excess of the oxide and a boiling soln. some silver periodate is formed. Mercuric oxide is slowly transformed into mercuric chloride and oxide; chlorine, oxygen, and possibly chlorine monoxide are evolved. Aq. soln. of the trichloride give a precipitate of iodine with a little stannous chloride; with more stannous chloride, some stannous iodide is formed. Consequently, although chloroform extracts no iodine from the aq. soln., it will do so after the addition of stannous chloride. Sulphur dioxide and ferrous sulphate are oxidized.

Iodine trichloride resembles the monochloride in forming a series of addition products; these can be regarded as derivatives of the acid $ICl_3.HCl$, that is $HICl_4$. E. Filhol[22] made a series of these salts of the type $ICl_3R'Cl$—where R stands for Cs, Rb, K, Na, Li, NH_4, $N(CH_3)_4$—by leading chlorine into an aq. soln. of the iodide; or by adding iodine to an aq. soln. of the chloride. The salts crystallize readily, without water of crystallization, excepting that the sodium salt has two and the lithium salt four molecules of water of crystallization. A. Werner likens them to the salts of chloroauric acid:

$$\left[\begin{matrix}Cl\\ ClICl\\ Cl\end{matrix}\right]R' \qquad\qquad \left[\begin{matrix}Cl\\ ClAuCl\\ Cl\end{matrix}\right]R'$$

Pentahalides. Chloroaurates.

R. F. Weinland and F. Schlegelmilch also obtained a series of salts of the general formula $2ICl_3.RCl_2.8H_2O$, mostly in needle-like crystals—when R represents cobalt the crystals are dark orange-red; nickel, green; manganese, orange-red; zinc, golden yellow; beryllium, yellow; magnesium, yellow; and calcium or strontium, yellow. Salts with R=Ba, Cd, Cu, Hg, Pb were not obtained. The salts are not very stable; they decompose in a desiccator in a few days owing to the volatilization of iodine trichloride and water. They decompose rapidly when heated. In another series of salts of the type $ICl_3.R'Cl.nH_2O$, where R' represents univalent K, NH_4, Rb, Cs, Na, Li, and $N(CH_3)_4$, A. Werner says that "since iodine can be extracted from the salts by carbon tetrachloride, these salts must be addition products of RCl and ICl_3." The argument is not sound if it be intended to prove that these products are molecular compounds as distinct from compounds of the formula $R(ICl_4)$, because it could be argued that they are decomposed by this solvent: $R(ICl_4)\rightleftharpoons ICl_3+RCl$. Several other polyhalides of this kind have been reported.[23] P. Jaillard described a compound $SCl_2.2ICl_3$; and R. Weber, $SCl_4.ICl_3$. O. Ruff

and G. Fischer obtained golden yellow crystals of $SCl_4.2ICl_3$ by leading chlorine into a cold soln. of the trichloride in sulphur chloride. The compound easily decomposes.

E. Beckmann and F. Junker [24] obtained the value 233 for the mol. wt. of iodine trichloride when dissolved in phosgene—the theoretical value for ICl_3 is 233·4. G. Oddo found the depression of the f.p. of soln. of the trichloride in phosphoryl oxychloride corresponded with a mol. wt. 134·21 to 173·42 ; the calculated value for the trichloride is ICl_3, and hence the trichloride must be dissociated or ionized —G. Oddo thinks ionized $ICl_3 \rightleftharpoons ICl_2{}^{\cdot}+Cl'$; in water the mol. wt. 42·0 to 46·2 also represents decomposition. P. Walden found the electrical conductivity measurements of soln. of the trichloride in liquid sulphur dioxide, arsenic trichloride, and sulphuryl chloride corresponded with an ionization which increased with increased dilution. The temp. coeff. of the conductivity is negative ; with sulphuryl chloride soln. a chemical change obscured the results. G. Oddo and E. Serra found the b.p. of carbon tetrachloride to be lowered, not raised, with iodine trichloride as solute. This was attributed to the volatilization of the trichloride at the b.p. of the solvent. The mol. wt. calculated from the depression of the f.p. of soln. in glacial acetic acid approximated with increasing dilution to 120, that is half the value required for ICl_3 ; this is attributed to the dissociation $ICl_3 \rightleftharpoons ICl+Cl_2$, and possibly also ionization. P. Schützenberger [25] regarded the trichloride as a molecular compound of the mono- and penta-chlorides $ICl.ICl_5$; J. Philipp supposed it to be a molecular compound of the monochloride and chlorine, $ICl.Cl_2$; G. Oddo, as a salt similar in constitution to $(C_6H_5)_2{=}I{-}Cl$, and $C_6H_5{-}I{=}Cl_2$; and H. Stanley as a compound of univalent iodine with tervalent chlorine :

$$I{-}Cl{<}^{Cl}_{\vdots\atop Cl}$$

Iodine and bromine.—In his historic memoir on bromine, A. J. Balard (1826) [26] said :

> Iodine appears to be capable of forming with bromine two different compounds. By taking iodine with a certain proportion of bromine, a solid is produced which, when heated, furnishes reddish-brown vapours, which condense into small fern-like crystals of the same colour. A further addition of bromine transforms these crystals into a liquid compound which has the appearance of hydriodic acid.

C. Löwig confirmed the observations of A. J. Balard, and assumed that the liquid rich in bromine corresponded with IBr_3, and the one poor in bromine, with IBr. H. Lagermarck made a crystalline solid by mixing eq. amount of the two elements ; and W. Bornemann also made the same compound by adding a slight excess of bromine, and volatilized the excess of bromine by heating the product at 50° in a stream of inert gas. The product when cold formed a hard crystalline mass, the colour of iodine, and whose composition corresponds with **iodine monobromide,** IBr. J. B. Hannay also made the monobromide by the action of iodine monochloride on sulphur dibromide : $2ICl+S_2Br_2=2IBr+S_2Cl_2$; and L. von Ilosvay made it by the action of bromine vapour on alkyl iodides.

Iodine monobromide forms dark grey crystals resembling iodine and smelling of bromine. The physiological action of the vapour is similar to that of bromine. By slow sublimation at 50° it may be obtained in fern-like crystals 2 cm. long. According to P. C. E. M. Terwogt,[27] the sp. gr. of the solid is 4·4157 (0°), 4·4135 (10°), 3·7616 (42°), and 3·7343 (50°). When the sp. vol. or sp. gr. of mixtures of iodine and bromine at different temp. are plotted against the composition, the curves are continuous except where there is a change of state from solid to liquid ; and the curvature is concave upwards from the concentration axis, showing that there is a contraction which may be due either to the formation of a compound or to some physical cause. The heat of formation, according to M. Berthelot, is $I_{solid}+Br_{liquid}$

$=IBr_{solid}+2.47$ Cals., and with all the constituents solid, $+2.34$ Cals. According to K. Strecker, between 99·7° and 214·5°, the sp. ht. of the vapour is $C_v=0.039$, $C_p=0.029$; and the ratio of the two sp. ht. varies from 1·325 to 1·411—mean 1·33. It is, however, doubtful if these results refer to anything but the dissociated vapour, *i.e.* to a mixture of the vapours of iodine and bromine. The m.p. of the monobromide is near 42°, the lower values which have been reported are due to the presence of impurities; the b.p. is near 116°, although it volatilizes at a lower temp. than this. The liquid rich in bromine formed by the action of bromine on the monobromide has been styled *iodine tribromide*, IBr_3, and *iodine pentabromide*, IBr_5. C. Löwig mixed the liquid with a little water, and allowed it to stand in the cold; the yellowish-brown crystals which separated were said to be *hydrated iodine pentabromide*. W. Bornemann showed that in all probability these crystals are a mixture of ice and iodine bromide; he also tried to prepare a higher bromide than IBr, but failed, the reddish-brown liquid obtained by the action of bromine on the monobromide when cooled furnished crystals of the monobromide and an excess of bromine.

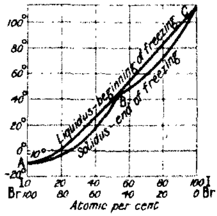

FIG. 27.—Freezing Point Curves of Mixtures of Iodine and Bromine.

In 1907, P. C. E. M. Terwogt[28] investigated the system iodine-bromine, and showed that the liquidus and solidus f.p. curves, Fig. 27, of mixtures of iodine and bromine nearly coincide when the ratio I : Br=1 : 1, while with all other mixtures there is an unbroken series of mixed crystals, in the one case, *AB*, between iodine monobromide and an excess of bromine, and in the other case, *BC*, between iodine monobromide and an excess of iodine. The coincidence of the liquidus and solidus curves at the point *B* shows a high degree of probability that a single individual is present in the system. P. C. E. M. Terwogt also investigated the b.p. curves and obtained two curves, one representing the percentage (atomic) composition of the liquid, and the other that of the vapour at the b.p. of the liquid. Some results are shown in Table XII. The general shape of the f.p. curves is that indicated in Fig. 27, but the curves do not approach one another so closely as in the case with iodine and chlorine corresponding with the fact that at the b.p., bromine monochloride is probably dissociated more than the corresponding iodine monochloride. This is in harmony with W. Bornemann's observation that iodine monobromide cannot be distilled between 90° and 100° without some decomposition—the distillate indeed contains so much bromine in excess that it remains liquid. The accumulation of bromine in the vapour phase correspond with the greater volatility of that element. The vap. press. at 50·2° and 92·8° are as follows:

TABLE XII.—BOILING POINTS OF MIXTURES OF IODINE AND BROMINE.

Atomic per cent. of iodine.		B.p. and barometric press.
Liquid.	Vapour.	
0	0	58·7° (771·2 mm.)
20	2·08	72·7° (759·3 mm.)
47·17	8·25	104·3° (756·3 mm.)
52	27·06	126·0° (750·0 mm.)
60	42·90	145·4° (708·8 mm.)
80	50·32	159·4° (757·8 mm.)
100	100	187·5° (771·7 mm.)

TABLE XIII.—VAPOUR PRESSURES OF IODINE-BROMINE MIXTURES.

Temp. 50·2°.			Temp. 92·8°.		
Atomic per cent. of iodine.		Vap. press. mm.	Atomic per cent. of iodine.		Vap. press. mm.
Liquid.	Vapour.		Liquid.	Vapour.	
25	0	331·0	50	0	372·0
50	8·23	86·1	70	27·38	160·5
100	100·00	3·5	100	100·00	30·7

J. J. von Laar has shown how the form of the vap. press. curves of a liquid mixture can furnish an indication, not a precise computation, of the degree of dissociation of any compound which may be formed, on the assumption that the different kind of molecules in the liquid—I_2, Br_2, and IBr—possess partial press. each of which is equal to the product of the vap. press. of a given component in the unmixed state and its fractional molecular concentration in the liquid. It is assumed that in the liquid, there is a balanced reaction $2IBr \rightleftharpoons I_2+Br_2$, to which the law of mass action applies, where K is the equilibrium constant, and C_1, C_2, and C respectively denote the concentration of the free iodine, free bromine, and iodine bromide. From this, P. C. E. M. Terwogt infers that at 50·2°, K for the liquid is $\frac{1}{74}$; and that for iodine monobromide about 20 per cent. of the liquid and about 80 per cent. of the vapour is dissociated. That the vapour of iodine monobromide is not quite dissociated into its elements is evident from its absorption spectrum, which shows some fine red orange and yellow lines in addition to those which characterize iodine and bromine. In thin layers, the colour of the vapour is copper red. O. Ruff [29] could not prove the formation of a compound by the measurements of the light absorption of soln. of iodine and bromine in carbon tetrachloride.

Iodine monobromide has a specific electrical conductivity of $3·078\times10^{-4}$ reciprocal ohms when liquid at 40·6°, and $6·51\times10^{-4}$ when solid at 16·3°. The iodine collects at the cathode, and the bromine at the anode when melted bromine monoiodide is electrolyzed between silver electrodes.[30] Iodine monobromide dissolves in chloroform, ether, and alcohol, forming reddish-brown soln. According to E. Solly, the ethereal soln. is electrically conducting, but not the soln. in sulphur chloride, S_2Cl_2, or carbon disulphide. Iodine monobromide is hydrolyzed by water, the liberated iodine colours the soln. brown, and some iodine may be precipitated. Indigo soln. are decolorized; and starch paste is coloured reddish-brown. According to P. Walden, the molecular conductivity of soln. of the monobromide in liquid sulphur dioxide, arsenic trichloride, and sulphuryl chloride increases with dilution; the simultaneous soln. of bromine and iodine in these solvents raises the conductivity more than the additive sum of the constituents in the same solvent; and the conductivity of a mixture I+4Br is greater than that of I+2Br, possibly because of the formation of iodine tribromide. The conductivity decreases with a rise of temp. and conversely.

Iodine monobromide, like the other binary halogen compounds, has the faculty of forming polyhalides additively. They are obtained by the soln. of the halogen halide in a conc. soln. of the alkali halide salts. Thus, H. L. Wells and S. L. Penfield [31] prepared KBr.IBr, CsCl.IBr, CsBr.IBr, RbBr.IBr, etc. Since $CsBr_2I$ is more stable than $CsBrI_2$, it follows that it is the mutual affinity of the halogens themselves, rather than the volatility of the contained halogen, which determines the stability.

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CHAPTER XVIII

THE COMPOUNDS OF THE HALOGENS WITH HYDROGEN

§ 1. The Preparation of Hydrogen Fluoride and Hydrofluoric Acid

HYDROGEN fluoride rarely occurs free in nature; but its presence has been detected in the effluvia from vents in volcanic districts; for example, R. V. Matteucci[1] found it in the gaseous products of the fumeroles of Vesuvius. Hydrogen fluoride is formed by the direct union of the elements; and by the action of fluorine on water, ammonia, hydrocarbons, and many organic compounds. It is also formed by the action of steam on some of the metal fluorides—lead fluoride, silver fluoride, etc.—and by the action of some fluorides on water—*e.g.* iodine pentafluoride. The fluorides and fluosilicates are decomposed by sulphuric acid, with the evolution of hydrogen fluoride—the reaction is incomplete with hydrochloric acid in place of sulphuric acid. G. Gore used chromic fluoride and sulphuric acid; R. Luboldt decomposed cryolite with the same acid.

An aq. soln. of hydrofluoric acid is prepared in the laboratory by the process recommended by J. L. Gay Lussac and L. J. Thénard (1809),[2] in which fluorspar is heated with sulphuric acid in lead or platinum vessels. The reaction is represented: $CaF_2+H_2SO_4=CaSO_4+2HF$. The fluorspar should be as free from silica as possible to prevent the formation of hydrofluosilicic acid: $6HF+SiO_2=2H_2O+H_2SiF_6$. Up to 80 per cent. of the theoretical yield can be obtained with sulphuric acid containing about 10 per cent. of water; with a more conc. acid, the yield is less; with sulphuric acid containing about 50 per cent. of sulphur trioxide, fluosulphuric acid, $HFSO_3$, distils over; and with sulphuric acid containing 60 per cent. of sulphur trioxide, almost pure fluosulphuric acid collects in the receiver. In any case, some calcium fluosulphonate, $Ca(FSO_3)_2$, is always found in the residue in the retort.[3]

On a manufacturing scale, an aq. soln. of hydrofluoric acid is made by gently heating the best quality of powdered fluorspar, free from silica, to about 130° along with conc. sulphuric acid—containing 10 per cent. of water. The retort is a cast-iron pot with a cast-iron cover. The rim of the cover dips into an annular trough; the joint is sealed with conc. sulphuric acid. The retorts are connected with a series of lead boxes as condensers. These contain water or dil. hydrofluoric acid to absorb the gas from the retorts. The condensers are submerged in water to keep them cool, and the acid so obtained is collected in leaden bottles.

Commercial hydrofluoric acid always contains sulphuric and hydrofluosilicic acids; and generally iron; arsenic; lead; and sulphurous acid. Some hydrogen sulphide may be present if the fluorspar contained lead or iron sulphide. According to C. F. Stahl,[4] commercial samples, examined over a period of five years, contained from 33·5 to 54·2 per cent. of hydrofluoric acid; 2·7 to 14·9 per cent. of hydrofluosilicic acid; and up to 1·9 per cent. of free sulphuric acid. The hydrofluosilicic acid can be almost all removed by the addition of a little aq. soln. of potash, and the redistillation of the liquid decanted from the precipitated potassium fluosilicate. G. Gore removed the arsenic, lead, etc., by diluting the acid until it contained less then 40 per cent. HF, and passed hydrogen sulphide through the liquid. The free hydrogen sulphide is then removed by the addition of silver carbonate or oxide. and the clear decanted liquid re-distilled. T. E. Thorpe and F. J. Hambly destroyed the

sulphurous acid by treating the acid with potassium permanganate before distillation. H. Moissan purified hydrofluoric acid from silica by neutralizing one quarter of a given volume of hydrofluoric acid with an alcoholic soln. of potassium hydroxide, or better, potassium carbonate prepared from the purified bicarbonate. The two portions were mixed, and distilled in a lead retort heated on an oil-bath at 120°. Potassium fluosilicate is not decomposed at this temp., and the acid collected was free from silica.

According to E. Frémy's *Recherches sur les fluorures* (1856), the acid furnished by the action of sulphuric acid on fluorspar always contains water, sulphuric acid, sulphurous acid, hydrofluosilicic acid, and other impurities. After many fruitless attempts to purify and dehydrate the crude material so obtained, he sought other means of preparation, and found that anhydrous hydrofluoric acid could be satisfactorily obtained by heating well-dried potassium hydrogen fluoride in a platinum retort attached to a platinum receiver which was cooled by immersion in a freezing mixture. The first portions of the acid which distilled over contained a little moisture. H. Moissan thus describes the operation :

The dry acid salt was placed as quickly as possible in a platinum retort previously heated to redness so as to free it completely from moisture. The salt was first heated for about an hour to a moderate temp. so that only a slight decomposition occurred, the small quantity of acid distilling over during this preliminary heating, which contained any traces of water absorbed during the manipulation of the salt, was allowed to escape. A platinum receiver was next fitted to the retort, which was then more strongly heated, but only to a temp. sufficiently high to decompose the salt slowly; the receiver was cooled by a mixture of ice and salt as indicated in Fig. 1. From the moment of cooling the receiver all the hydrofluoric acid was condensed to a limpid liquid, boiling at 19·5°. Hydrofluoric acid thus obtained sometimes contains a small quantity of alkaline fluoride, carried over by the acid vapours during the decomposition of the salt. If it is desired to obtain pure hydrofluoric acid free from this salt, a large platinum retort must be used, and the acid vapours must be led to the condenser through a long platinum tube sloping upwards from the retort, and kept above the temp. at which the acid boils.

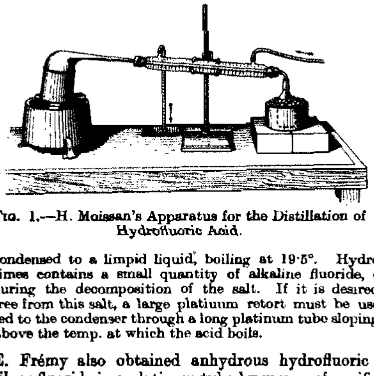

FIG. 1.—H. Moissan's Apparatus for the Distillation of Hydrofluoric Acid.

E. Frémy also obtained anhydrous hydrofluoric acid by decomposing lead or silver fluoride in a platinum tube by means of purified and dry hydrogen.

Anhydrous hydrofluoric acid is so hygroscopic that H. Moissan said that he found it could be kept in the anhydrous condition only with the greatest difficulty. G. Gore, and T. E. Thorpe and F. J. Hambly recommended keeping anhydrous acid in platinum bottles with a ground platinum plate sealed with paraffin wax, and held in place by a clamp. This plan is too expensive for ordinary work, and ceresine wax bottles are generally used. For transport, the commercial acid is bottled and sealed in lead, guttapercha, paraffin, or ceresine wax vessels. The acid attacks vulcanized caoutchouc.[5]

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§ 2. The Properties of Hydrogen Fluoride and Hydrofluoric Acid

Experiments with hydrogen fluoride and conc. hydrofluoric acid are extremely dangerous owing to the volatility and extremely corrosive nature of the vapour. The vapour causes an intolerable pricking, burning sensation; and if a drop of the conc. acid comes in contact with the skin it produces serious, painful, ulcerated sores. An incautious inhalation of the vapour may so affect the membrane of the throat, that a temporary loss of voice may be produced: C. J. Knox (1840) thus lost his voice permanently during his early experiments on the electrolysis of the acid. H. Davy is said to have abandoned his attempts to isolate fluorine because of the risks. It is said that P. Louyet (1850) and F. J. Nicklès (1869) died from the effects of accidentally inhaling the vapour of the conc. acid. If a little acid accidentally comes in contact with the skin, washing the affected part immediately with water and then with dil. aq. ammonia is effective with the dil. acid. Very dil. acid—up to say 5 per cent.—produces no ill effect by temporary contact with the skin. With the more conc. acid—say 60 per cent.—the ammonia treatment does not prevent inflammation, and C. F. Stahl recommends continuing the washing of the affected part for half an hour under flowing water when "the bad effects will be prevented or at least materially reduced." The washing should begin immediately after the acid has come in contact with the skin.

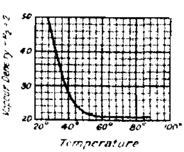

FIG. 2.—Vapour Density of Hydrogen Fluoride.

Hydrogen fluoride is a colourless transparent gas which can be condensed to a colourless mobile liquid which fumes strongly in air. The **vapour density** of the gas[1] at 21·4° ($H_2=2$) is 51·18 (or 1·773, air=1); and it diminishes rapidly as the temp. rises until, at 90°, it is 20·58. This is illustrated by the graph, Fig. 2. The lower number corresponds with a mol. wt. HF. Hence, at 90°, hydrogen fluoride contains two atoms. At lower temp. the molecule polymerizes to H_nF_n. There is, however, nothing to show what the molecules are. They *may* be partly HF, partly H_2F_2, H_3F_3, etc. The facts only permit the statement that below 90° gaseous hydrogen fluoride is a mixture of molecules, H_mF_m, H_nF_n, . . . where the values of m, n, . . . are unknown. Other evidence to be discussed later leads to the assumption that there is a state of equilibrium, $H_2F_2 \rightleftharpoons 2HF$, at each temp. If so, the relative proportions of the two kinds of molecules can be calculated from the vapour density at a given temp. Similar results are obtained by lowering the press. and keeping the temp. constant at, say, 32°. Judging by the **boiling points** of its family relations, which decrease with decreasing mol. wt., HI, −35·5°; HBr, −67·1°; HCl, −83·4°, the b.p. of hydrogen fluoride might be expected to fall below −83·4°; as a matter of fact, G. Gore[2] found the liquid to boil at +19·4°. This, said H. M. Vernon, probably means that the molecules of liquid hydrogen fluoride are more complex than is represented by the simple formula HF. The b.p. of the liquid, 19·4°, is very near the prevailing temp. of the atm. in temperate climes. Its vap. press. at 15·5° is 394 mm. The **specific gravity** of the liquid at 13·6° is 0·9885; at 12·8°, 0·9879; and at 11·1°,

0·9922. According to A. Guntz,[3] its **heat of vaporization** is 7·2 Cals. per mol. of HF. If the molecule is polymerized to H_2F_2, as appears probable from the vapour density determinations, the heat of vaporization will be $2\times7·24=14·48$ Cals. The quotient by Trouton's rule is then $14480\div292·4=49·5$—a value much higher than the normal. It is therefore assumed that much heat is spent in the work of depolymerization: $H_2F_2\rightarrow2HF$. According to M. Berthelot and H. Moissan,[4] the heat of formation of this compound from its elements is $H_{gas}+F_{gas}=HF_{gas}+38·6$ Cals.; or $H_{gas}+F_{gas}=HF_{liquid}+45·8$ Cals. The liquid solidifies if cooled to about $-102·5°$, forming a white opaque solid which has a **melting point**[5] $-92·3°$. As indicated previously, liquid hydrogen fluoride is a **non-conductor of electricity.**[6]

Hydrofluoric acid like water is an associated liquid, and even the gas, as we shall soon see, is associated. It has the power of uniting with fluorides. It also seems to be an ionizing solvent for a soln. of potassium fluoride in liquid hydrogen fluoride is an excellent conductor; it also possesses marked solvent powers. According to E. C. Franklin,[7] the liquid readily dissolves potassium fluoride, chloride, and sulphate; sodium fluoride, bromide, nitrate, chlorate, and bromate; acetamide; and urea. The solvent action is not so marked with barium fluoride, cupric chloride, and silver cyanide; while calcium and lead fluorides; copper sulphate and nitrate; ferric chloride, mercuric oxide, and magnesium metal, are virtually insoluble in this menstruum. Glass also is not affected by the liquid if moisture be absent. The liquid scarcely acts on most of the metals or non-metals at ordinary temp., though it does act on the alkali metals at ordinary temp., much the same as does water, with the simultaneous production of flame.

The properties of hydrofluoric acid.—Hydrogen fluoride is soluble in water between 0° and 19·4° in all proportions. The aq. soln. forms hydrofluoric acid; the more conc. solutions fume strongly in air. The **specific gravity** of aq. soln. increases with increasing concentration of hydrogen fluoride up to a maximum 1·262 with soln. containing 75·93 per cent. of HF, and then decreases to unity as the concentration increases. The numbers in Table I are calculated from those of J. L. C. Eckelt,[8] and of E. G. Hill and A. P. Sirkar. The table shows that the sp. gr. of a 63 per cent. soln. is 1·246 at 0°. Table II is due to C. Winteler. The contamination of the soln. with hydrofluosilicic acid greatly increases the density.

TABLE I.—SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF HYDROFLUORIC ACID WITH UP TO 99 PER CENT. OF HF—AT 0°.

	0	1	2	3	4	5	6	7	8	9
0	1·000	1·003	1·006	1·010	1·014	1·019	1·023	1·026	1·029	1·033
1	1·037	1·040	1·044	1·048	1·052	1·056	1·060	1·064	1·069	1·073
2	1·077	1·083	1·086	1·090	1·093	1·097	1·100	1·104	1·107	1·111
3	1·114	1·118	1·121	1·125	1·128	1·132	1·136	1·139	1·142	1·146
4	1·149	1·153	1·157	1·161	1·165	1·169	1·174	1·179	1·184	1·189
5	1·195	1·200	1·205	1·211	1·216	1·221	1·225	1·239	1·232	1·235
6	1·238	1·241	1·243	1·246	1·248	1·249	1·250	1·252	1·253	1·254
7	1·256	1·257	1·259	1·260	1·261	1·261	1·262	1·259	1·256	1·253
8	1·250	1·246	1·242	1·239	1·235	1·230	1·224	1·219	1·211	1·199
9	1·180	1·161	1·140	1·123	1·102	1·082	1·065	1·049	1·033	1·016

A. A. Bineau[9] found that during the boiling of a conc. aq. soln. of hydrofluoric acid an excess of hydrogen fluoride escapes until there remains a soln. with a constant b.p., 130°, and a constant composition corresponding with about 36 per cent. HF. In an analogous way, if dil. soln. are distilled, the first fractions are particularly rich in water, this continues until there remains an acid with the same constant b. temp, and the same constant composition. Similarly, if the conc. or dil. acid is allowed to stand over slaked lime, the former becomes more dil. and the latter more conc.

until the same residue—about 36 per cent. HF; b.p. 120°—is obtained. A. A. Bineau supposed that this constant remainder represented a definite hydrate $HF.2H_2O$; but H. E. Roscoe has shown that this is probably a mistaken inference, since the composition of the residue varies with the press.

TABLE II.—SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF HYDROFLUORIC ACID WITH UP TO 50 PER CENT. OF HF—AT 20°.

	0	1	2	3	4	5	6	7	8	9
0	—	1·003	1·007	1·011	1·014	1·018	1·023	1·027	1·030	1·035
1	1·038	1·041	1·045	1·049	1·052	1·055	1·059	1·062	1·066	1·069
2	1·072	1·076	1·049	1·052	1·086	1·089	1·092	1·095	1·098	1·101
3	1·104	1·106	1·119	1·112	1·114	1·117	1·120	1·122	1·125	1·127
4	1·130	1·133	1·136	1·138	1·141	1·143	1·146	1·149	1·152	1·154
5	1·157	—	—	—	—	—	—	—	—	—

P. Louyet thought that the acid which he made by the action of sulphuric acid on fluorspar was a hydrate, but there is no evidence of this. According to R. Metzner,[10] a 30 per cent. aq. soln. of hydrogen fluoride does not freeze at −70°, but at about −45°, the 43·4 per cent. "pure" acid of commerce gradually deposits small opaline masses. If the 55 per cent. acid be slowly cooled to −45°, it forms small truncated prisms with a composition corresponding with **monohydrated hydrogen fluoride,** $HF.H_2O$, and melting at −35°; the temp. of the melting mass remains constant until the change is complete. The crystals of the hydrate are said to fume in air, and to dissolve in cold conc. acid; the sp. gr. of the crystals is given as 1·15. The monohydrate readily forms supersaturated soln. There is no evidence of a dihydrate; and it must be added that the monohydrate is not yet to be regarded as definitely established. A. A. Bineau's constant boiling mixture, when frozen, has no definite m.p., and appears to be a mixture of ice and the monohydrate. The f.p. curve of the binary system $HF—H_2O$ has not been worked out. E. G. Hill and A. P. Sirkar obtained two maxima in their curve showing the molecular electrical conductivity of soln. of different concentration—one at about 91 per cent. HF, and the other between 51 and 55 per cent. HF. If these maxima represent definite compounds, the former would correspond with $HF.9H_2O$, and the latter with $HF.H_2O$.

G. Gore, in his early work, showed that the presence of hydrogen fluoride in water lowered its f.p. E. Paternó and A. Peratoner [11] measured the depression of the f.p. of water by soln. containing from 0·057 to 2·80 mol. per litre; and W. Ostwald showed that the results corresponded with the presence of molecules of HF, partially ionized, in the soln.

The **specific heats** of aq. soln. of hydrofluoric acid [12] is smaller the greater the concentration: with 5 per cent. of HF, 0·947; with 7·51 per cent. of HF, 0·925; 13·26 per cent. HF, 0·875; 20 per cent. HF, 0·840; and with 25·92 per cent. of HF, 0·798. The sp. ht. of the soln. is greater than that of the other mineral acids of eq. concentration. It has been suggested that this might be due to the absorption of heat during the ionization of the acid with rising temp.

The **heat of solution** of gaseous hydrogen fluoride [13] in an excess of water is $HF_{gas}+Aq.=11·8$ Cals.; and $HF_{liquid}+400H_2O=4·56$ Cals.; the heat of dilution of $HF+0·5\,H_2O$ to $400H_2O$ is 2·05 Cals.; of $HF+16·7H_2O$, 0·72 Cal.; of $HF+2·25H_2O$, 0·55 Cal.; of $HF+6·51H_2O$, 0·1 Cal.; and of $HF+12·03H_2O$, almost zero. The **heat of neutralization** [14] is $NaOH_{aq.}=16·272$ Cals., with $LiOH_{aq.}$, 16·4 Cals., and with $KOH_{aq.}$, 16·1 Cals.—these numbers are greater than those for the other three halogen acids, and about 4 per cent. larger than the heat of neutralization for sulphuric acid. If the soln. be exactly neutralized and a further quantity of hydrofluoric acid be added, much heat is absorbed—approximately 0·288 Cal. When

hydrofluoric acts similarly on sodium chloride, 0·100 Cal. is evolved; and with hydrochloric acid on sodium fluoride, 2·363 Cals. are absorbed. When one eq. of hydrochloric acid acts on an eq. of sodium fluoride, about 0·95 eq. of the latter is decomposed; while when one eq. of hydrofluoric acid acts on an eq. of sodium chloride, only 0·05 eq. of the latter is converted to the fluoride. Hence, argued J. Thomsen the *Avidität* of hydrofluoric acid is but 5 or 6 per cent. of that of hydrochloric acid. This result was not expected because the avidity of the related acids hydrochloric, hydrobromic, and hydriodic acids—increases as their mol. wt. decreases; and hydrofluoric acid has the smaller avidity. This result is confirmed by E. Deussen's work [15] on the effect of these acids on the speed of inversion of cane sugar to invert sugar, and on the esterification of the alcohols. Hydrofluoric acid is about 17 times less active than hydrochloric acid; and it is rather less active than phosphoric acid. These results are also in agreement with the smaller **electrical conductivity** [16] and small ionization constant of this acid. If v denotes the number of litres containing a mol. of HF, μ_0 the electrical conductivity at 0°, and μ_{25} that at 25°, α, the degree of ionization, is equal to μ/μ^∞; and the ionization constant K is equal to $\alpha^2/(1-\alpha)v$. E. Deussen's results are:

v . . .	1	2	4	16	64	256	1024
μ_0 . .	18·94	20·42	23·57	36·60	61·55	105·8	173
μ_{25} . .	21·46	26·17	29·88	46·37	80·70	140·8	230
α . . .	0·062	0·067	0·076	0·118	0·205	0·36	0·58
K . .	0·00410	0·00241	0·00156	0·000987	0·000826	0·000791	0·000782

A comparison of these values of α with those for the other haloid acids, will show how little this acid is ionized in aq. soln. For example, the molecular electrical conductivities for the four haloid acids, at 25°, are

v	HF	HCl	HBr	HI
4	29·6	366	377	376
32 . . .	59·5	393	398	397
1024 . . .	224·0	—	405	404

The ionization constants $K_{25}=0·00065+0·000025(1-\alpha)/\alpha$; and $K_0=0·00090+0·00007(1-\alpha)/\alpha$. The acid is only half ionized even when but a mol. is present in a litre of soln. The inconstancy of K particularly with the more conc. soln. up to $v=4$ is noteworthy. The **heat of ionization** at about 19° and a concentration of 3·6 litres per mol. is $HF=H^{\cdot}+F'+2·57$ Cals.

P. Walden concludes that in dil. aq. soln. hydrofluoric acid is a feebly ionized monobasic acid, HF. G. Pellini and L. Pegoraro [17] conclude from their conductivity measurements that the molecules of hydrogen fluoride or of the normal fluorides are not polymerized to H_2F_2-molecules in aq. soln.: but the conductivity of the acid with successive additions of sodium, potassium, or ammonium hydroxide shows a maximum when acid eq. to half a mol. of hydrofluoric acid has been added, and there is an abrupt change in the slope of the conductivity curve when an eq. of alkali has been added. This behaviour is characteristic of dibasic acids; hence it might be assumed that hydrofluoric acid is dibasic H_2F_2. Again, with the reaction: $HgO+2HF\rightleftharpoons HgF_2+H_2O$ in aq. soln., the concentrations of the H_2O and of the solid HgO may be regarded as constant. If C denotes the concentration of the HgF_2, and C_1 that of the HF assumed to exist in soln. as non-associated HF, the equilibrium conditions will be $C=k_1C_1^2$ where k_1 is constant; while if the equilibrium condition be $HgO+H_2F_2+H_2O$, and C_2 denotes the concentration of the hydrofluoric acid, assumed to be polymerized, H_2F_2, the equilibrium condition will be $C=k_2C_2$, where k_2 is constant. The observations of A. Jäger agree better with the latter hypothesis than with the former. Hence, A. Jäger concluded that the molecules of hydrofluoric acid are present in the form H_2F_2. R. Abegg drew a similar conclusion from the action of hydrofluoric acid on boric acid. According to W. Ostwald's rule, the electrical conductivity of the sodium salts of monobasic acids rises about 10 units on dilution from a concentration $v=\frac{1}{32}N$ to $v=\frac{1}{1024}N$, and with dibasic

acids about 20 units. Thus, the conductivity of the sodium salt at 25° is 104·0 for $v=\frac{1}{24}$, and 93·0 for $v=\frac{1}{32}$, the difference $104-93=11$ is in harmony with the assumption that a monobasic acid is in question. R. Kremann and W. Decolle found that the rise of the conductivity of the sodium salt of hydrofluoric acid agrees with the assumption that this is a dibasic acid, H_2F_2. E. Deussen has attempted to reconcile the conflicting opinions by assuming that hydrofluoric acid is neither an out-and-out mono- nor a di-basic acid, but rather occupies *eine Zwischenstellung*. H. Pick (1912) suggests that the apparent anomaly is explained qualitatively and quantitatively by assuming that there is no appreciable association of the molecules to H_2F_2, the ionization constant K at 25° agrees with $HF \rightleftharpoons H^{\cdot}+F'$ in dil. soln. when $K=[H^{\cdot}][F']/[HF]=0{\cdot}00072$. In the more conc. soln. where K varies very much with concentration, the HF molecules unite with the F'-ions forming a complex HF_2', which has the equilibrium constant $[HF_2']/[H^{\cdot}][F']=5{\cdot}5$, corresponding with the balanced reaction $HF+F' \rightleftharpoons HF_2'$. With these assumptions H. Pick has estimated the relative concentrations of the HF molecules and of the $H^{\cdot}$ and HF_2' ions of soln. of different concentration; and he has shown that the calculated electrical conductivities then agree satisfactorily with the observed values. The results are graphed in Fig. 3 against the normality of the soln.

The majority of the following qualitative results were recorded by G. Gore,[18] or by H. Moissan. Hydrofluoric acid attacks nearly all the metals—gold and platinum metals resist attack; copper and silver are slowly attacked; iron and zinc are rapidly dissolved. A mixture of hydrofluoric and nitric acids dissolves boron, silicon, columbium, tantalum, etc., but not gold, platinum, diamond, silicon carbide, etc. Silica is dissolved and converted partly into silicon tetrafluoride, and partly into hydrofluosilicic acid, H_2SiF_6. Similar remarks apply to many of the silicates, *q.v.* Most metal oxides are attacked by the acid. Most of the oxides are transformed into fluorides and in many cases dissolved. According to G. Gore, the higher oxides of cerium, iron, manganese, lead, silver, tin, and thallium, and the monoxides of cobalt, nickel, and tin, are not attacked. Calcined alumina and corundum are not decomposed by conc. hydrofluoric acid. Phosphorus pentoxide reacts with hydrogen fluoride; J. W. Mallet[19] thought that phosphorus pentafluoride, PF_5, was formed, but H. Moissan showed that phosphorus oxyfluoride, POF_3, is the product of the reaction. In consequence, phosphorus pentoxide cannot be used for drying the gas. Sulphurous, vanadic, arsenious, and molybdic oxides are rapidly decomposed. The action of hydrofluoric acid on various oxides has been studied by W. K. van Haagen and E. F. Smith.[20] They passed the vapours of hydrofluoric acid over the certain oxides heated in a platinum boat, and found alumina at a high temp. is converted into fluoride; cerium, yttrium and lanthanum oxides at a red heat form a non-volatile fluoride or oxyfluoride; zirconia and zirconium minerals, titanium, tantalum and columbium oxides and the minerals at a red heat form volatile fluorides; thorium dioxide was slightly attacked; potassium dichromate lost nearly all its chromium, sodium tungstate lost only part of its tungsten; sodium phosphate lost all its phosphorus; and cassiterite was only slightly attacked. A. Jäger has studied the action of hydrofluoric acid on mercuric, cupric, and lead oxides; E. Deussen measured the solubility of iron, cupric, and lead oxides in this acid, and also the solubility of iron scale in aq. hydrofluoric acid; and E. R. Zalinsky has studied the solubility of the iron ores—magnetite, ilmenite, hæmatite, iron pyrites, and chromite in this acid. The iodides, bromides, and chlorides of the

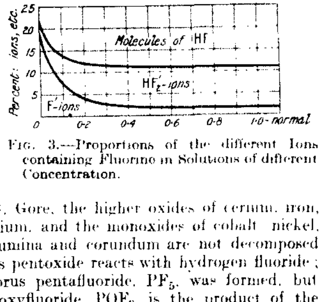

FIG. 3.—Proportions of the different Ions containing Fluorine in Solutions of different Concentration.

alkali and alkali earth metals are decomposed with the liberation of iodine, bromine, or chlorine as the case might be. The iodides of zinc, cadmium, lead, mercury, silver and platinum, and cuprous, arsenious, and antimonous iodides are not decomposed; and the bromides of zinc and cadmium are only slightly attacked. Titanic, phosphorous, and antimonous chlorides are decomposed. The chlorides of chromium, cadmium, manganese, nickel, cobalt, lead, copper, mercury, and silver are not decomposed. The liquid chlorides of carbon, phosphorus, sulphur, arsenic and gold, and chromyl chloride do not mix with the acid. The fluosilicates, fluotitanates, and fluoborates of the alkali metals are decomposed.

R. F. Weinland and O. Lauenstein[21] found that periodic acid, potassium chlorate, bromate, and permanganate crystallize unchanged from a 40 per cent. of the acid. According to G. Gore, moist crystals of potassium permanganate give a green liquid. The iodates of the alkaline earths and of nickel give the corresponding fluorides, and the alkali iodates furnish fluo-oxyiodates, MIO_2F_2. The nitrates of the alkalies, alkaline earths, lead, and uranyl are decomposed; silver nitrate does not appear to be attacked. Calcium phosphide is decomposed, copper phosphide not so. Ammonium, calcium, uranium, and copper are wholly or partially dissolved. The carbonates, sulphates, and borates are decomposed. The sulphides of the alkalies and alkaline earths are decomposed; while the sulphides of arsenic, antimony, molybdenum, zinc, cadmium, tin, iron, lead, copper, mercury, and palladium are not attacked. Cobalt sulphate is not attacked, while the sulphates of the alkalies and alkaline earths are attacked and dissolved. Alkali tungstates, ammonium arsenite and arsenate, copper arsenite, ammonium magnesium arsenate, ammonium molybdate and vanadate, potassium cyanide and ferrocyanide are decomposed. Paraffin is not attacked; shellac, gum arabic, gum tragacanth, copal, etc., are decomposed. Celluloid is slowly attacked. Silk paper, gun cotton, gelatin, parchment are dissolved. M. Meslans[22] has studied the esterification of alcohol by hydrofluoric acid.

The composition and molecular weight of hydrogen fluoride.—G. Gore[23] measured the volume of hydrogen required to form hydrogen fluoride when heated with silver fluoride. He found that 100 volumes of hydrogen furnished nearly 200 volumes of hydrogen fluoride. The deviations from the ideal volume relations just indicated were attributed by G. Gore to the "partial condensation of the hydrofluoric acid to the liquid state." Representing the reaction: $H_2+2AgF=2HF+2Ag$, he accordingly inferred that hydrogen fluoride contains half its own volume of hydrogen, and half its own volume of fluorine. The formula is therefore H_nF_n. The vapour density at 100° corresponds with the molecule HF; the vapour density at lower temp. than 80° shows that the molecule polymerizes. G. Gore's results were confirmed by H. Moissan, who measured the relative amounts of fluorine and oxygen liberated during the electrolysis of hydrofluoric acid. The volume of the hydrogen was measured directly the fluoride gas was passed into water, and the corresponding volume of oxygen: $2H_2O+2F_2=4HF+O_2$, was measured. On the assumption that two volumes of fluorine liberated one volume of oxygen, the calculated and observed results agreed very well with the assumption that hydrogen fluoride is formed by the union of equal volumes of the two gases. H. Moissan also allowed a measured volume of fluorine to act on water; he measured the volume of oxygen produced, and determined the hydrofluoric acid by titration. Here again the results confirmed the conclusion of G. Gore that two volumes of hydrogen fluoride are produced by the union of one volume of hydrogen and one of fluorine. For example, 12·5 c.c. of fluorine furnished 6·40 c.c. of oxygen, and 24·49 c.c. of hydrogen fluoride; the calculated values were 6·25 c.c. of oxygen, and 25·00 c.c. of hydrogen fluoride. As already indicated, the peculiar properties of hydrogen fluoride and of the acid agree with the assumption that under certain conditions the molecule is HF, and under other conditions H_2F_2.

The use of hydrofluoric acid and the fluorides.—Hydrofluoric acid attacks quartz and siliceous substances, glass, etc., forming silicon fluoride: SiO_2+4HF

$=SiF_4+2H_2O$, and it is accordingly used in the analysis of silicates. When most silicates are repeatedly evaporated with hydrofluoric and sulphuric acids, all the silica is volatilized as silicon fluoride, etc., and the residue of sulphates can be examined by the standard methods. The use of hydrofluoric acid in certain analytical separations has been discussed by A. A. Noyes, L. W. McCay, N. H. Furman, etc.[24]

One of the most important properties of hydrofluoric acid is for etching glass and porcelain. Glass may be etched with the gas or with an aq. soln. of the gas. In the former case, the etching appears opaque and dull; in the latter case, shining and transparent. For etching, the glass is covered with a film of wax, and the design to be etched on the glass is drawn on the surface with a stylus; or else the parts of the glass not to be etched are coated with a resistant varnish. The surface is exposed to the action of the acid or gas, and very soon the glass is etched. The wax or varnish is then washed off with turpentine. The corrosive action of the hydrogen fluoride is due to the ready decomposition of the glass in contact with hydrogen fluoride. The silica forms silicon fluoride. The process is used for marking the scales on glass instruments, etc. A soln. of 32 per cent. ammonium fluoride in 20 per cent. hydrofluoric acid is known in commerce as *white acid*; it is used for frosting electric bulbs, etc.

The use of hydrofluoric acid has been recommended in the filling of silk, and for the cleaning many articles from siliceous materials—the grime from buildings and monuments in industrial towns, etc. It has been recommended for pickling iron and brass castings so as to free them from sand.[25] It has been suggested for the purification of graphite; but it proved too expensive an agent for removing silica and silicates from anthracite for making electrical carbons. J. Effront [26] recommends the use of very dil. soln. of the acid in preparing alcoholic liquids from cereals to retard the development of certain injurious bacteria; ammonium fluoride is used in the sterilization of the vessels and rubber hose in the fermentation industries. It has been suggested as a means of removing alkalies from the juice of sugar beets.[27] It is used in preparing hydrofluosilicic acid. Antimony acid fluoride is used in dyeing. The fluosilicates are used in hardening artificial plasters. Hydrofluoric acid or a fluoride is used in the coagulation of rubber latex.[28] The former is added to the electrolyte in one process for the preparation of antimony,[29] and it has also been employed in the electrolytic oxidation process—*e.g.* electrolytic preparation of chlorates and persulphates. A dil. soln. of the acid has also been recommended for opening petroleum and natural gas borings where the free passage has been blocked.

Detection and determination of the fluorides.—The metal fluorides are decomposed by treatment with conc. sulphuric acid, and the reaction is attended by the evolution of hydrofluoric acid which etches glass, furnishes the so-called *etching test for fluorides*. The substance under examination is warmed with sulphuric acid in a leaden vessel covered with a watch-glass. The watch-glass is coated with wax, and a design ✠ is scratched with a pin or knife, so as to expose the glass to the action of the acid. The wax is afterwards removed, and if the design is etched on the glass, it is inferred that fluorides were present. The test will indicate the presence of 0·0003 grm. of calcium fluoride. Many silicates contain combined fluorine in a form which does not give hydrofluoric acid by treatment with hot sulphuric acid—*e.g.* topaz, tourmaline, etc. The fluorine in these minerals must be transformed into calcium fluoride before the test is applied. To do this, the powdered mineral is fused with about eight times its weight of sodium carbonate. The cold cake is extracted with water. An excess of ammonium carbonate is added, and the precipitate filtered off—preferably after the mixture stood overnight. The soln. is evaporated to a small volume and neutralized with hydrochloric acid using phenolphthalein as indicator; when boiled, the phenolphthalein colour may reappear. The process is repeated until this is not the case. Calcium fluoride is added and the soln. boiled. A mixture of calcium chloride and carbonate is precipitated. This is washed, dried, and ignited in a platinum dish. The residue is treated with dil. acetic acid; evaporated to dryness; leached with water; and the undissolved

calcium fluoride is collected on a filter paper, and washed. The filter paper is burnt from the dried precipitate, and the residue is ready for the test. A similar procedure is adopted in determining the fluorine in minerals, since the calcium fluoride can be weighed and the corresponding amount of fluorine calculated.

Silver nitrate gives no precipitate with soln. of soluble fluorides; both calcium and barium chlorides give precipitates in alkaline soln. The precipitation may not occur if a large proportion of an ammonium salt is present. The precipitates are sparingly soluble in mineral acids and in acetic acid Ferric chloride gives a white *precipitate of a complex fluoride analogous in composition to cryolite.* Fluorine in soln. as alkali fluoride is readily precipitated as thorium fluoride, $ThF_4.H_2O$, in the cold, by adding thorium nitrate to the soln. slightly acidified with nitric or acetic acid. An excess of thorium nitrate should be avoided since it is slightly soluble therein. The washed precipitate can be dried, ignited, and weighed as thorium oxide, and the amount of fluorine calculated.[30] If the powdered fluoride be mixed with an excess of sand, and heated in a test-tube with sulphuric acid, silicon fluoride, SiF_4, is formed. If a drop of water at the end of a glass rod be held in the upper part of the test-tube, a white film of silicic acid will be formed over the surface of the water owing to the decomposition of the silicon fluoride by the water: $3SiF_4+3H_2O=H_2SiO_3+2H_2SiF_6$. There is also a method of measuring the amount of silicon fluoride in a gas burette, and calculating the corresponding amount of fluorine. The free acid can be titrated with alkali using phenolphthalein, rosalic acid, or methyl orange as indicator.[31]

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§ 3. The Fluorides

The fluorides are prepared by the action of hydrofluoric acid upon the metals, metal oxides, hydroxides, carbonates, etc. Fluorine gas also acts on a great many elements and their compounds producing fluorides ; but fluorine is not a convenient reagent in the laboratory or works. In some cases, the fluorides can be obtained by the action of the liquid hydrogen fluoride on the proper chloride, and the product fractionally distilled—*e.g.* the fluorides of tin, titanium, and antimony.[1] If hydrogen fluoride be passed over heated oxide of aluminium, lanthanum, zirconium, tantalum, niobium, or cerium, the corresponding fluoride is formed as condensable vapour.[2] Arsenic pentafluoride forms arsenic and the metal fluoride when passed over the heated metals—copper, zinc, iron, bismuth, lead, mercury.[3] The fluosilicates or fluoborates also convert some metal oxides—with or without carbon—into the fluorides.[4] Some fluorides are formed by double decomposition, but this is not usual since double salts are generally produced. Arsenic or antimony fluoride[5] converts tungsten chloride, WCl_6, into the corresponding tungsten fluoride: $WCl_6+2AsF_3=2AsCl_3+WF_6$. Silver fluoride converts phosphoric, phosphorous, phosphoryl, silicon, or boron chloride into the corresponding fluoride and silver chloride.[6] Ammonium fluoride—solid or in soln.—converts many metal salts in soln. into the corresponding fluorides.[7]

The fluorides of the non-metallic elements are usually gaseous at ordinary temp.—*e.g.* the fluorides of phosphorus, arsenic, silicon, and boron, and carbon tetrafluoride. Those which are solid melt easily, and closely resemble the corresponding chlorides, bromides, and iodides. The metal fluorides often volatize without decomposition. The fluorides of the alkali metals, silver, tin, and antimony, are soluble in water ; the fluorides of the metals of the alkaline earths are sparingly soluble. Silver fluoride dissolves in about half its weight of water, and in this respect it differs in a remarkable way from the silver salts of the other three halogens. The very sparing solubility of calcium fluoride is also in marked contrast with the behaviour of the corresponding salts of the other halogens. Soln. of the alkali fluorides on evaporation lose acid, and acquire an alkaline reaction ; and some of the hydrated fluorides when heated give off part of their water, and the other part is given off along with some hydrogen fluoride. The fluorides are generally very stable and are not decomposed when heated alone or admixed with carbon. Silver fluoride, says E. Frémy, is not decomposed by heat, and mercuric fluoride volatilizes unchanged. The fluorides of the heavy metals are usually decomposed when heated with hydrogen, but not

fluorspar. Oxygen does not act on silver fluoride either at 15° or at 600°; fluorspar is partly decomposed at a high temp. in a stream of oxygen. Lead fluoride can be sublimed unchanged in oxygen. Many fluorides are decomposed if heated in a current of steam *e.g.* fluorspar, cryolite, silver fluoride, lead fluoride, etc. Conc. nitric or sulphuric acid decomposes most of the fluorides forming hydrofluoric acid, and the respective nitrates or sulphates; hydrogen chloride also decomposes most of the fluorides, wholly or partially, when they are heated in a stream of the gas; according to H. St. C. Deville,[8] the fluorides of zirconium, chromium, and aluminium resist this treatment. Fluorspar is decomposed when heated in a stream of carbon disulphide, forming calcium sulphide. Many fluorides are decomposed by fused microcosmic salt: $CaF_2+NaPO_3+H_2O=NaCaPO_4+2HF$; when heated with silica: $4AgF+SiO_2=4Ag+O_2+SiF_4$; and when fused with silica and sodium carbonate; with alkali bisulphates; or with boric acid or the borates.

Acid fluorides.—J. J. Berzelius, and later E. Frémy[9] in his *Recherches sur les fluorures* (1856), showed that the fluorides have a great tendency to form readily crystallizable compounds with hydrofluoric acid—the so-called acid fluorides. H. Moissan, and E. Eggeling and J. Meyer, for example, have prepared the acid fluorides of potassium, rubidium, and cæsium of the type MF.HF, MF.2HF, and MF.3HF; and E. Böhm made a series of acid fluorides of mercury, copper, nickel, and cobalt with combined water *e.g.* $NiF_2.6H_2O.5HF$. The heavy metals form acid fluorides resembling those of the alkali metals and ammonium. Thus, freshly precipitated mercuric oxide dissolves in conc. hydrofluoric acid, and the soln. evaporated over sulphuric acid, in vacuo, gives monoclinic crystals which have a composition corresponding with mercurous acid fluoride, $HgF.2HF.2H_2O$; copper, cobalt, and nickel oxides or carbonates treated in a similar way furnish the corresponding acid fluorides, $RF_2.5HF.nH_2O$. When the nickel or copper salt is treated with ammonia the salts, $CuF_2(NH_3)_45H_2O$ and $5NiF_2(NH_3)_68H_2O$, are formed; while the mercury salt gives mercuric amidofluoride, $NH_2—Hg—F$, and the cobalt salt gives $CoF_2.2NH_4Cl.2H_2O$. Difluorotetramminocobaltic chloride, $Co(NH_3)_4F_2Cl$, and hexamminocobaltic fluoride, $CO(NH_3)_6F_3$, have been made by the action of hydrofluoric acid upon tetramminodicarbonatocobaltic chloride, and luteocobaltic chloride respectively.

Double or complex fluorides.—The fluorides also unite among themselves to form complex or double fluorides, and thus are formed the fluoborates, $KF.BF_3$, or KBF_4; the fluosilicates, $2KF.SiF_4$, or K_2SiF_6; the fluoaluminates, $3NaF.AlF_3$—of which the mineral cryolite is the typical example; fluocuprates, $2KF.CuF_2$, or K_2CuF_4; and numerous others. P. Barteczko[10] has compiled the following list of these salts which were known up to 1900; the symbols in brackets represent compounds which are known only in combination with hydrogen fluoride. The list will be extended as new compounds are prepared. It does not follow that this list will be curtailed with increasing knowledge since many products formerly thought to be chemical individuals are now considered to be mixtures or solid soln.

Univalent elements.

Li	Na	NH_4	K	Rb	Cs	Ag	Hg	Tl
[LiF_2M]	[NaF_2M]	[NH_4F_2M]	[KF_2M]	[RbF_2M]	[CsF_2M]	[AgF_2M]	—	[TlF_2M]
—	—	—	[KF_3M_2]	[RbF_3M_2]	—	[AgF_3M_2]	[HgF_3M_2]	—
—	—	—	[KF_4M_3]	[RbF_4M_3]	—	[AgF_4M_3]	—	—

Bivalent elements.

Ca	Mg	Be	Zn	Cd
—	MgF_3M	BeF_3M	—	CdF_2M
[CaF_4M_2]	MgF_4M_2	BeF_4M_2	ZnF_4M_2	—

Cu	Fe	Co	Ni	Sn
—	FeF_3M	CoF_3M	NiF_3M	—
CuF_4M_2	FeF_4M_2	CoF_4M_2	NiF_4M_2	SnF_4M_2
CuF_7M_5	—	CoF_7M_5	NiF_7M_5	$Sn_3F_8M_2$

Tervalent elements.

B	Sb	Bi	Al	Di	La
BF_4M	SbF_4M	—	AlF_4M	DiF_4M	
BF_5M_2	SbF_5M_2	—	AlF_5M_2	—	
—	SbF_6M_3	[BiF_6M_3]	AlF_6M_3	DiF_6M_3	
—	Sb_2F_7M	—	AlF_7M_4	Di_2F_7M	—
—	$Sb_3F_{10}M$	—	Al_2F_7M	$Di_4F_{15}M_3$	$La_2F_9M_3$
—	$Sb_4F_{13}M$	—	$Al_2F_9M_3$	—	
	$Sb_7F_{25}M_4$	—	$Al_3F_{11}M_2$	—	—
—	—	—	$Al_3F_{14}M_5$	—	—

Fe	Cr	Mn	U	V	Ti
FeF_4M	—	MnF_4M	—	VF_4M	—
FeF_5M_2	CrF_5M_2	MnF_5M_2	—	VF_5M_2	TiF_5M_2
FeF_6M_3	CrF_6M_3	—	—	VF_6M_3	TiF_6M_3
$Fe_2F_9M_3$	$Cr_2F_9M_3$	—	$UF_{11}M_8$	$V_2F_{11}M_5$	—

Quadrivalent elements.

Te	Si	Ge	Sn	Ti	Zr
TeF_5M	—	—		—	ZrF_5M
—	SiF_6M_2	GeF_6M_2	SnF_6M_2	TiF_6M_2	ZrF_6M_2
—	SiF_7M_3	—	—	TiF_7M_3	ZrF_7M_3
—	—	—	SnF_8M_4	TiF_8M_4	ZrF_8M_4
—	—	—			Zr_2F_9M
—	$Si_3F_{17}M_5$	—		—	$Zr_2F_{13}M_5$
—	—	—	—	—	$Zr_3F_{14}M_2$
—	—	—		—	$Zr_3F_{17}M_5$

Ce	Mn	Pb	Th	U
—	—	—	ThF_5M	UF_5M
—	MnF_6M_2	—	ThF_6M_2	UF_6M_2
—	—	PbF_8M_4	—	—
$Ce_2Fl_{11}M_3$	—	—	—	—

Quinquevalent elements.

As	Sb	Nb	Ta
—	SbF_6M	—	TaF_6M
AsF_7M_2	SbF_7M_2	NbF_7M_2	TaF_7M_2
—	—	—	TaF_8M_3
—	—	$NbF_{10}M_5$	—
	—	$NbF_{12}M_7$	$TaF_{20}M_{15}$

In 1869, C. W. Blomstrand[11] attempted to explain the molecular structure of these compounds by assuming the halogen to be bivalent. This would make potassium acid fluoride K—F—F—H. It is considered more probable that fluorine is uni-, ter-, quadri-, or septa-valent. in harmony with the corresponding variable valency of the other halogens. This would make the graphic formula of potassium acid fluoride. cryolite, etc.:

$$K-F=F-H \qquad Hg{<}\begin{matrix}F-M\\F-M\end{matrix} \qquad \begin{matrix}F\\F\end{matrix}{>}B-F=F-K \qquad \begin{matrix}F\\F\end{matrix}{>}Si{<}\begin{matrix}F=F-K\\F=F-K\end{matrix} \qquad Al\begin{matrix}\diagup F=F-Na\\ -F=F-Na\\ \diagdown F=F-Na\end{matrix}$$

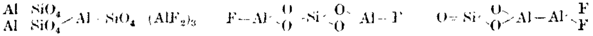
A. Werner, in his *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (Braunschweig, 68, 1905),[12] assumed that in the double halides, the halogen atoms are united to the central atom so that the group acts as an acid anhydride. The compounds above symbolized then become:

$$[F.K.F]H \qquad \left[F.Hg\begin{matrix}.F\\.F\end{matrix}\right]M \qquad \left[\begin{matrix}F.\\F.\end{matrix}B\begin{matrix}.F\\.F\end{matrix}\right]K \qquad \left[\begin{matrix}F. & .F\\F.Si.F\\F. & .F\end{matrix}\right]K_2 \qquad \left[\begin{matrix}F. & .F\\F.Al.F\\F. & .F\end{matrix}\right]Na_3$$

where M stands for a univalent radicle. Accordingly, the halogen atoms act as intermediate or connecting links between two elementary atoms. There are also some mixed halogen salts in which fluorine is replaced by one or other of the three halogens.

Oxy- and hydroxy-fluorides.—In still another group of fluorides part of the

fluorine may be replaced by oxygen to form a group of compounds called *oxyfluorides*; in some cases, too, hydroxyl groups may replace the fluorine to form *hydroxyfluorides*. In the topazes, fluorine and hydroxyl appear to be isomorphous, for the relative proportions of the two radicles –F and OH– vary; in minerals poorest in fluorine the ratio F : OH is nearly as 3 : 1. Although several formulæ have been suggested for a typical topaz *e.g.*



it is supposed that one or more fluorine atoms per molecule can be replaced by hydroxyl, OH.

The oxyfluorides also unite with other fluorides to form *double or complex* oxyfluorides. P. Barteczko appended to his list of double fluorides the following table of the principal types of the double oxyfluorides:

BiO^{I}	MnO^{II}	VO^{II}	TiO_2^{II}
$(BiO)F_3M_2$	$(MnO)F_4M_2$	$(VO)F_4M_2$	$(TiO_2)F_4M_2$
	—	$(VO)F_5M_3$	$(TiO_2)F_5M_3$
	—	$(VO)_3F_{13}M_4$	$(TiO_2)F_6M_2$
—	—	$(VO)_3F_{14}M_8$	$(TiO_2)F_7M_3$
—		$(VO)_4F_{15}M_7$	—

Quinquevalent elements.

AsO^{III}	MoO^{III}	VO^{III}	VO_2^{I}	NbO^{III}
$(AsO)F_4M$	$(MoO)F_5M_2$	$(VO)F_5M_2$	$(VO_2)F_3M_2$	$(NbO)F_4M$
—	$(MoO)_3F_{14}M_5$	$(VO)_2F_9M_3$	$(VO_2)F_4M_3$	$(NbO)F_5M_2$
		—	$(VO_2)F_5M_4$	$(NbO)F_6M_3$
		—		$(NbO)F_7M_4$
			—	$(NbO)_3F_{13}M_4$
—		—	—	$(NbO)_3F_{14}M_5$

NbO^{I}	TaO^{III}
$(NbO_2)_3F_5M_2$	$(TaO)F_6M_3$
—	$(TaO)F_7M_4$

Sexivalent elements.

MoO_2^{II}	WO_2^{II}	UO_2
$(MoO_2)F_3M$	$(WO_2)F_3M$	$(UO_2)F_3M$
$(MoO_2)F_4M_2$	$(WO_2)F_4M_2$	$(UO_2)F_4M_2$
$(MoO_2)F_5M_3$	$(WO_2)F_5M_3$	$(UO_2)F_5M_3$
$(MoO_2)F_{11}M_9$	—	$(UO_2)F_6M_4$
—	—	$(UO_2)_2F_7M_3$
—	—	$(UO_2)_2F_9M_5$
—	—	$(UO_2)_2F_{10}M_6$

W. Werner drew attention to the fact that the elements which show a tendency to form oxyfluorides occupy neighbouring positions in the periodic table of D. I. Mendeléeff, *viz.*

Ti	V	Cr
Zr	Nb	Mo
—	Ta	W

to these elements can be added uranium, iodine, and boron. The two latter do not appear in P. Barteczko's list. There is the potassium oxyfluoborate, $B_2O_3(FK)_2$, of H. Schiff and R. Sestini[13] (1884); and the alkali and ammonium oxyfluoiodates, $O_2IF_2M_2$, where M represents Na, K, Rb, Cs, or NH_4—prepared by R. F. Weinland and O. Lauenstein (1897). A. Werner's O_3CrF_2M, is also omitted from P. Barteczko's list.

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§ 4. Equilibrium, and the Kinetic Theory of Chemical Action

. . . The streaming atoms
Fly on to clash together again, and make
Another and another state of things
For ever . . .

REJECTED ADDRESSES.

All the halogens unite with hydrogen forming compounds of the type HX, where X represents an atom of the halogen. With fluorine the reaction proceeds explosively in the dark, even at as low a temp. as −252·5°. At ordinary temp. chlorine and hydrogen unite in light, not in darkness, and the union occurs with explosive violence if a mixture of the two gases be sparked, or lighted with a taper. These same two gases also unite in the presence of platinum foil, platinum black, or charcoal.[1] When a mixture of equal parts of iodine or bromine and hydrogen gases is passed through a red-hot tube, or, better, over finely divided platinum, or platinized asbestos, or charcoal, some hydrogen iodide, HI, or hydrogen bromide, HBr, is formed as the case might be. If hydrogen iodide gas be treated in a similar way, some iodine and hydrogen are produced. In each case, if the temp. of the tube be 440°, we have approximately 80 per cent. of hydrogen iodide, and 20 per cent. of a mixture of equal volumes of iodine and hydrogen. The only apparent effect of the catalytic agent—platinized asbestos, etc.—is to accelerate the reaction, and if these agents be absent, the time required to make 80 per cent. of hydrogen iodide from the mixture of hydrogen and iodine is much longer. Once this proportion of hydrogen iodide has been formed, the composition of the exit gases remains unchanged, however long the mixture may be heated at 440°, with or without the catalytic agents.

Bimolecular reaction.—In the bimolecular reaction $A+B\rightleftharpoons M+N$, let C_A and C_B respectively denote the concentrations of the substances A and B, expressed in mol. per litre. Similarly, let C_M and C_N respectively denote the concentrations of M and N. It has previously been shown that the speed of the reaction is equal to the product of the affinity or the driving force of the reaction, k, and the concentrations of the reacting substances, that is, the velocity of the reaction $A+B$ is equal to kC_AC_B. If A and B are the same, so that $2A\rightleftharpoons M+N$, the speed of the $\rightarrow$ reaction at any instant will be represented by kC_A^2. When hydrogen iodide dissociates: $2HI\rightleftharpoons H_2+I_2$. The speed of the $\rightarrow$ reaction at any instant will be represented by kC_{HI}^2; and the speed of the $\leftarrow$ reaction by $k'C_IC_H$. When equilibrium occurs, the speeds of these two reactions are the same, and therefore the **condition of equilibrium** is $kC_{HI}^2=k'C_HC_I$, or $K=k/k'=C_HC_I/C_{HI}^2$. At 440°, when the system is in equilibrium, nearly 20 per cent. of the hydrogen iodide will have dissociated. Hence, at 440° (80 per cent.) $2HI\rightleftharpoons H_2+I_2$(20 per cent.). This means that if 100

mol. of hydrogen iodide be heated to 440°. in a closed vessel, twenty will have dissociated when the system is in equilibrium. Hence $C_{HI}=80=C_{HI}^2=6400$; and $C_I=C_H=10$. Hence, $K=\frac{1}{64}$; or $C_{HI}^2=64C_HC_I$. This means that at 440°, when the concentration of the hydrogen and iodine is unity, these gases will combine 64 times as fast as hydrogen iodide of unit concentration will dissociate. It will be observed that each of the direct and reverse reactions is a **bimolecular reaction** because two molecules are involved in each operation. M. Bodenstein[2] found the decomposition of hydrogen iodide by heat proceeds as a bimolecular reaction: $2HI \rightleftharpoons H_2+I_2$; and in light, as a unimolecular reaction: $HI \rightleftharpoons H+I$, so that the mechanism of the two reactions is different.

The kinetic theory of chemical action.—The kinetic theory gives an interesting view of chemical action. Imagine a vessel filled with a mixture of equal volumes of iodine and hydrogen gases. The molecules of hydrogen and iodine must be continually crashing together. *A certain proportion* of these collisions will be **chemically fruitful** and result in chemical change. In the earlier stages of the reaction, the number of collisions per second between the hydrogen and iodine molecules will be relatively great, but later, as the hydrogen iodide accumulates, *the number of collisions between the hydrogen and iodine molecules will become* fewer and fewer, and accordingly, the speed of formation of hydrogen iodide will become less and less. The law of mass action can be deduced from the kinetic theory of gases as shown by J. J. Thomson[3] in his memoir *The Chemical Combination of Gases*.

Similarly, when two hydrogen iodide molecules crash together, a *certain proportion* of the collisions will result in a dissociation, so that an iodine and a hydrogen molecule will result. At first, the number of these collisions will be few and far between, but, as hydrogen iodide accumulates in the system, the number of collisions between these molecules will increase. Finally, when the number of chemically fruitful collisions per second between the iodine and hydrogen molecules is equal to the number of chemically fruitful collisions between the hydrogen iodide molecules, the system will subsequently undergo no perceptible change. Obviously, this does not mean that chemical action has ceased. Every time the proper molecules collide under the right conditions, hydrogen iodide will be formed or dissociated. Both changes proceed with the same velocity, and consequently the composition of the gas as a whole does not alter. Although it is said that when two opposing reactions are in equilibrium, the system is at a standstill, the apparent equilibrium is not a state of real tranquillity and repose. **Equilibrium is essentially dynamic and active, not static and passive.** It is possible to say that a chemical system is in equilibrium only when its composition does not change with the lapse of time.

If all the molecules of a reacting substance are alike, why do they not all undergo change at the same instant? What regulates the speed of the reaction in such a way that only a certain fraction of the total number of molecules changes in a given time? At first sight it seems that if all the molecules are in the same condition, then, either no chemical change will take place at all, or else all the molecules in a uniform mixture of two gases, which can react with one another, must undergo transformation at the same instant. The answer returned by the kinetic theory is somewhat as follows: According to the kinetic theory, the average velocity of the molecules becomes greater and greater as the temp. rises; and that although the *average* velocity is constant at any particular temp., the velocities of the faster-moving molecules may finally become so great that the crash, on collision, displaces the atoms from their position of equilibrium in the molecules. Take the case of water, H_2O. A rise of temp. not only accelerates the movements of translation of the molecules themselves, but it probably also increases the amplitudes and the velocities of the cyclic motions of the atoms within the molecule. The atomic movements may become so violent that the atoms of one or both molecules are thrown out of the sphere of one another's attraction, and it is no longer possible for the hydrogen and oxygen molecules in the swifter molecules to remain combined.

In other words, the molecules are dissociated. The dissociation of the gas is only partial, because the faster-moving molecules break down first. There is a kind of struggle for existence; the slower-moving molecules are the fittest to survive. It is, however, still possible for the atoms of hydrogen and oxygen to unite each to each forming elementary molecules H_2 and O_2; but if a still higher temp. be applied, even these combinations become unstable, and the two-atom molecules dissociate into one-atom molecules, for the atoms themselves then become mutually independent free-rovers.

It is not likely that mere shock on collision, or that mere speed of molecular motion, is sufficient to determine chemical action, the selective attraction of the atoms of the paired colliding molecules must play an essential part. A. Kekulé[4] assumed that the first phase in a chemical reaction is the juxtaposition of the molecules involving the formation of what he called a loosely-jointed polymolecule, and that the component atoms of the coupled molecules undergo rearrangement and take up positions compatible with the formation of stable systems. When the one-atom molecules collide, they enter the sphere of one another's attraction, and, if the velocities of the colliding molecules be not too great, the atoms may remain in contact re-forming a two-atom molecule. As before, when the speeds of dissociation and re-combination are equal, the system is in equilibrium.

Dissociation and combination are partial and incomplete.—As the temp. rises, the average velocity of the molecules of a gas become greater and greater. Although the *average* velocity of the molecules of a gas is constant at any temp., the velocities of *individual* molecules must vary considerably because of collisions, etc. It is possible that collisions between the *faster-moving molecules* of hydrogen iodide, alone, result in dissociation: $2HI = I_2 + H_2$; and that collisions between the slower-moving molecules of hydrogen iodide do not produce dissociation: similarly, it may be that collisions between the *slower-moving molecules* of hydrogen and iodine alone result in the formation of hydrogen iodide; and collisions between the fastest molecules do not lead to chemical action. Hence we can see how but a certain proportion of the collisions are chemically fruitful. This view of the action leads to several other interesting inferences, but since direct proof of the fundamental hypothesis is wanting, sufficient has been given to indicate the trend of modern thought.

The action of stimulants—contact action.—The speed of dissociation of hydrogen iodide at 518° is augmented threefold by raising the press. from 0·5 to 2 atm. The tremendous condensation of gases on the surfaces of such substances as platinized asbestos, platinum black, charcoal, etc., shows that the layer of gas near the surfaces of these substances must be very conc. E. Mitscherlich (1843)[5] estimated that when gaseous carbon dioxide is condensed on wood charcoal in layers about 0·005 mm. thick, the gaseous layer is nearly as dense as liquid carbon dioxide. Hence, it follows that the concentration of the molecules of one or both the reacting gases must be very great near the surface of the catalytic agent; and since the temp. is not altered, the average speed of the molecules will be the same; accordingly, the total number of collisions, and the number of chemically fruitful collisions in unit time, will be augmented. This means that the speeds of formation and dissociation of hydrogen iodide will be stimulated in the presence of such substances as platinized asbestos, etc. In other words, these substances act as catalytic agents.

A catalytic agent can alter the speed of a chemical action, but it cannot alter the condition of equilibrium.—Although the speed of a chemical reaction is modified by the presence of a catalytic agent, the final state of equilibrium is not affected. If otherwise, J. H. van't Hoff showed that we could allow these substances to react alternately with and without the catalytic agent; this would involve a change in the quantity combined, and the energy thus obtained could be made to do work. This would lead to perpetual motion, which is assumed to be impossible. This deduction has been confirmed experimentally with hydrogen iodide with and without platinum black. Hence, adds W. Nernst, the catalyst must always affect

the velocity of the reverse reaction. If the added substance increases the speed of formation of a substance, it must equally increase its velocity of decomposition.

A given reaction may proceed at different rates in different solvents. Thus, N. Menschutkin[6] found that the velocity of the reaction $N(C_2H_5)_3+C_2H_5I=N(C_2H_5)_4I$ is nearly a thousand times as fast in benzyl alcohol as it is in hexane as solvent. H. von Halban and A. Kirsch found the decomposition of xanthogenic acid, $HSSCOC_2H_5=CS_2+C_2H_5OH$, is nearly a million times as fast in alcohol as it is in carbon disulphide; both these solvents are decomposition products of the reactions. Similarly, J. T. Cundall found the dissociation of nitrogen peroxide, N_2O_4, when gaseous is nearly a hundred times as fast as when dissolved in chloroform. If it be right to assume that in each case the solvent at the end of the reaction remains in the same condition as at the beginning, the solvent can be regarded as a catalytic agent. For by definition a catalytic agent is one that inaugurates or alters the speed of a reaction without itself being changed in amount or kind at the end of the reaction. When a solvent acts catalytically, its mass is relatively large; the more striking examples of catalysis are those in which a relatively minute proportion of the catalytic agent produces great effects.

W. D. Bancroft expressed the opinion that something has been overlooked in J. H. van't Hoff's thermodynamic demonstration, for if in contact catalyzes only those substances which are adsorbed by the solid catalyst are affected catalytically, the solid catalytic agent may be regarded as eq. to a solvent, and may therefore displace the equilibrium of the adsorbed reacting substances. If, further, the products of the reaction are not selectively adsorbed by the solid but immediately liberated as a gaseous phase, it follows that the equilibrium will appear to be displaced by the catalytic agent. O. Dimroth (1913) could detect no relation between any of the physical constants of solvents and their effect on the state of equilibrium of balanced reactions, but he considers that the phenomenon is related to the solubilities of the reacting molecules such that in the reaction $A\rightleftharpoons B$, if K is the equilibrium constant independent of the nature of the solvent, and if C_1 and C_2 denote the respective concentration of A and B and S_1 and S_2, their solubilities, instead of writing $C_1/C_2=$constant, he writes $C_1/C_2=K(S_1/S_2)$. This has been established for a few organic compounds, but in other cases the rule broke down.

The relative frequency of uni- and bi-molecular reactions.—Uni- and bi-molecular reactions are very much more frequent than more complex reactions involving three or more molecules. This applies more particularly to reactions in gaseous systems. The number of *binary* collisions per second must be very much greater than the number of simultaneous collisions between, say, *three* molecules.

The idea can perhaps be illustrated by supposing that n white, n black, and m red balls, mixed up in a bowl, represent a swarm of reacting molecules. We are taught in algebra that the probability of drawing, in a binary combination, a white and a black ball is $2n^2(2n+m)^{-1}(2n+m-1)^{-1}$; and the probability of drawing a black, white, and red ball is $6n^2m(2n+m)^{-1}(2n+m-1)^{-1}(2n+m-2)^{-1}$. The probability of the binary combination against the ternary combination is as $(2n+m-2)$ is to $3m$. If m is very small in comparison with n the probability in favour of the binary combination is very great. In one c.c. of gas at 0° and 760 mm., n is of the order 10^{19}.

By an application of the mathematical theory of probability (Bernoulli's theorem) to a swarm of reacting molecules, moving according to the postulates of the kinetic theory of gases, a relation similar to C. M. Guldberg and P. Waage's law of chemical equilibrium will be obtained, *viz.* if a reaction between a number of substances, say A, B, M, N, can be represented by the equation: $mA+nB\rightleftharpoons pM+qN$, and if the concentrations of the reacting substances be respectively denoted by [A], [B], [M], [N], then, when the system is in equilibrium, the concentrations of the reacting molecules will be so related that $k_1[A]^m[B]^n\rightleftharpoons k_2[M]^p[N]^q$, where k_1 and k_2 are constants; and the equilibrium constant $=k_2/k_1=K$. Consequently, S. V. Sjanoschentzky (1908)[7] was led to say: Guldberg and Waage's law is not an independent hypothesis, but is rather a logical consequence of the kinetic theory

of gases. This deduction is independent of any hypothesis as to the affinity of the reacting molecules, and hence it is probable that affinity does not exert any appreciable influence on the translatory movements of the unpaired molecules, but is only exerted momentarily when the atoms of the paired molecules during copulation are settling down into a condition of equilibrium. Similarly, it follows that the so-called affinity constants k_1 and k_2 in C. M. Guldberg and P. Waage's equation include at least two factors, one of which is dependent on and the other independent of the affinity between the reacting molecules.

When several molecules are involved in a chemical process: (1) If the reaction is dependent on the juxtaposition of three or more reacting molecules, it is likely to be extremely slow; or (2) One or more intermediate reactions may be involved—one molecule, for instance, may unite with another molecule, and the pair (intermediate compound) later collide and react with a third molecule (consecutive reaction); or (3) The reaction may be localized in the vicinity of a solid where the reacting molecules form a dense layer and are comparatively close together (contact action).

The effect of temperature on equilibria.—Chemical reactions generally proceed more quickly at high than at low temp. D. Amato[8] says a mixture of hydrogen and chlorine, cooled to −12°, does not react in light, even if exposed for hours to direct sunlight; and J. H. Kastle and W. A. Beatty found that in darkness hydrogen and bromine combine very slowly at 196°, and in sunlight, the change is rapid at 196° and slow at 100°. On the other hand, there are some reactions whose speed is diminished with a rise of temp., and others again in which the reaction is reversed by raising the temp. It is probable that when the speed of a reaction is slow enough for convenient measurement, the relative number of reacting or active molecules is small. The increase in the number of active molecules with temp. increases with the sp. ht. C_v and the increase in the speed of the reaction is greater the greater the value of C_v.

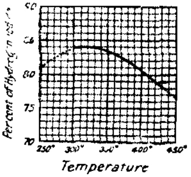

FIG. 4.—Effect of Heat on the Dissociation of Hydrogen Iodine.

The proportion of hydrogen iodide dissociated *decreases* with rise of temp. so long as the temp. does not exceed about 320°; above that critical temp., the higher the temp. the *greater* the amount of hydrogen iodide dissociated. This is illustrated by the graph, Fig. 4. The thermal value of the reaction changes sign at about the same critical temp.; for instance, at 18°, the union of hydrogen and iodine is an *endothermal* reaction: $H_2+I_2=2HI-6{\cdot}1$ Cals.; and at 520°, *exothermal*: $H_2+I_2=2HI+4{\cdot}4$ Cals. Experience shows that a rise of temp. always favours endothermal reactions. *When a system is in physical or chemical equilibrium a rise of temperature promotes the formation of those products which are formed with an absorption of heat; a rise of temperature resists the formation of those products formed with an evolution of heat; and a change of temperature has no effect on the equilibrium thermally neutral*—**J. H. van't Hoff's equilibrium law** (1884).[9] The law is a special case of the great principle of reversibility. If an exothermal reaction becomes endothermal at a high temp., there is a curious paradox: **A compound may be stable at temperatures exceeding that at which it dissociates.** The case of hydrogen iodide is particularly instructive. The change in the thermal value of the reaction corresponds with a change in the effect of a rise of temp. on the equilibrium. The quantitative side of this rule has already been discussed, and W. Nernst[10] has shown for the reaction $H_2+I_2=2HI$, the equation: $\log K=540{\cdot}4T^{-1}-0{\cdot}503\log T+2{\cdot}35$, represents the relation between the equilibrium and the absolute temp. T, in agreement with the observations of G. Lemoine (1877), P. Stegmüller (1907), M. Bodenstein (1894), and K. V. von Falckenstein (1910). For the equilibrium $H_2+Br_2\rightleftharpoons 2HBr$, the equation $\log K=5223T^{-1}-0{\cdot}533\log T-2{\cdot}72$ is similarly

employed for the observations of K. V. von Falckenstein (1910), and M. Bodenstein and A. Geiger (1904); and for the equilibrium $H_2+Cl_2 \rightleftharpoons 2HCl$, the equation $\log K = 9554T^{-1} - 0.553 \log T + 2.42$ is used for the observations of M. Bodenstein and A. Geiger (1904). *The comparison of the percentage degree of dissociation of* the hydrogen compounds of the three halogens in Table III, calculated by

TABLE III.—PERCENTAGE DISSOCIATION OF THE HYDROGEN HALIDES AT DIFFERENT TEMPERATURES.

Temperature $T°$ K.	Percentage dissociation.		
	HCl	HBr	HI
290°	2.51×10^{-15}	4.14×10^{-8}	6·2
500°	1.92×10^{-8}	2.91×10^{-4}	15·5
700	1.12×10^{-5}	9.93×10^{-3}	22·2
900°	3.98×10^{-4}	7.18×10^{-2}	27·0
1000°	1.34×10^{-3}	0·144	29·0
1500°	6.10×10^{-2}	1·19	—
2000°	0·41	3·40	—
2500°	1·30	—	—

F. Pollitzer, emphasizes how the tendency of the hydrogen halides to dissociation increases as the at. wt. of the halogen increases. At the higher temp., the results are complicated by the dissociation of the two-atom molecules of the halogen into *one-atom molecules. The free energy of the reaction* $\frac{1}{2}H_2+\frac{1}{2}I_{2\,gas}=HI$, at $T°$ K., according to F. Haber, is $-89.575-1.575T \log T+0.00549T^2-RT \log (P_{HI}/P_{I_2}P_{H_2})^{\frac{1}{2}} +2.67T$. The equation is not consistent with results obtained in other ways—possibly, as F. Haber suggested, owing to dissociation. G. N. Lewis and M. Randall give $-1340+0.000725T^2-2.48T$; and if solid iodine be used, $7110+3.35T \log T-0.00275T^2-41.845T$.

The principle applies to physical equilibria. When anhydrous sodium sulphate is dissolved in water, heat is evolved, and its solubility *decreases* with a rise of temp.; hydrated sodium sulphate dissolves in water with an absorption of heat, and its solubility *increases* with rise of temp. The vaporization of water is an endothermal reaction, and hence a rise of temp. favours vaporization, for it increases the concentration of the vapour phase.

The effect of pressure on equilibria.—The principle is also applicable to other forms of energy. Increasing the press. of a dissociating compound decreases the amount of dissociation, and this presumably relieves the strain set up by the increased press. Thus: *when a system is in a state of physical or chemical equilibrium, an increase of pressure favours the system formed with a decrease in volume; a reduction of pressure favours the system formed with an increase in volume; and a change of pressure has no effect on a system formed without a change in volume*—**G. Robin's law** (1879).[11] Thus, hydrogen iodide is formed from hydrogen and iodine without a change in volume, and the state of equilibrium is not affected by variations of press. When ice melts, the liquid occupies a smaller volume than an eq. amount of ice; and experiment shows that the m.p. of ice is lowered by press. in agreement with the law. With sulphur, the converse is true. The m.p. of sulphur is raised by press., but the liquid phase has a greater sp. vol. than the solid phase.

The principle of least effort.—The principle of least action underlies all these rules, and it is of great service, and of wide application. P. L. M. Maupertius foreshadowed the idea in 1747: All natural changes take place in such a way that the existing state of things suffers the least possible change; or, as W. D. Bancroft (1911) expressed it: **A system tends to change so as to minimize the effects of an external disturbing force.** This has been called the principle of the

opposition of reactions to further change, and it was stated in general terms by H. le Chatelier: *If a system in physical or chemical equilibrium be subjected to a stress involving a change of temperature, pressure, concentration, etc., the state of the system will automatically tend to alter so as to undo the effect of the stress*—**H. le Chatelier's law** (1888).[12] For instance, if the temp. of a system in equilibrium be raised a few degrees, the state of the system will change so as to induce the formation of that component or phase which absorbs most heat, and accordingly tend to lower the temp. If the → reaction be exothermal the change will proceed in the reverse direction; and if the → reaction be endothermal, the system will change in the same direction. Again, if the press. of the dissociating iodine I_2 (one vol.) ⇌ 2I (2 vols.) be increased, the state of the system will change so that the volume is diminished; and conversely, if the press. be reduced, the state of the system will change so that the volume is increased, that is, the less the press. the greater the amount of iodine dissociated. In the case of soln., an increase of concentration will induce the formation of that component or phase which will lower the concentration of the solute added; and an increase of vap. press. will lead to the formation of that component or phase which will reduce the vap. press., etc.

Again, in virtue of H. le Chatelier's rule that all compounds tend to change in such a way as to relieve the disturbing effects of the strain, W. D. Bancroft showed that light will tend to destroy all substances which absorb it—*e.g.* chlorine in a mixture of hydrogen and chlorine—and just as all compounds absorb light rays of a certain wave-length, so must all compounds be sensitive to such rays. The rule, however, gives no inkling whether the given stimulus will actually produce a change. Thus, no appreciable change takes place with copper sulphate; nor with chromium sulphate unless a catalytic agent be present; there is a visible decomposition with silver salts; and in some cases fluorescent or phosphorescent phenomena occur

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§ 5. The Union of Hydrogen and Chlorine in Light

On August 10th, 1801, W. Cruickshank[1] noticed the gradual combination of oxygenated muriatic acid (*i.e.* chlorine) with hydrogen, hydrocarbons, and carbon monoxide. He said :—

If the pure oxigenated muriatic acid, in the form of a gas, be mixed in certain proportions with any of these inflammable gases and introduced into a bottle filled with and inverted over water, *though no immediate action may be at first perceptible*, yet, in twenty-four hours a complete decomposition will be found to have taken place, the products varying according to the nature of the gases employed. . . . I introduced into a phial with a glass stopper, filled with and inverted over water, one measure of pure hydrogen and afterwards two measures of *very pure oxigenated muriatic gas, this* nearly filled the bottle; the stopper, was then introduced very tight under water, and before the stopper was introduced, a whitish cloud appeared in the mixture yet *very little or no diminution could be observed* . . . ; at the end of twenty-four hours when the stopper was withdrawn the whole of the gas instantly disappeared except about one-tenth of a measure, which was found to be azote, and must have been originally contained in the two measures of oxigenated muriatic acid and water, for the water in the phial contained common muriatic acid, but did not in the least smell of the oxigenated acid.

On February 27th, 1809, J. L. Gay Lussac and L. J. Thénard confined a mixture containing equal volumes of hydrogen and chlorine in darkness and another mixture in light for several days. The characteristic colour of the chlorine disappeared in

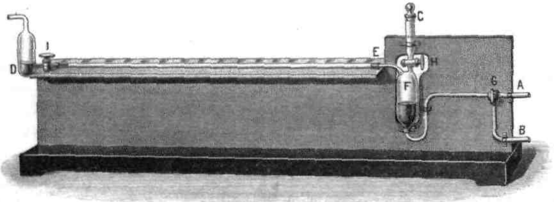

FIG. 5.—Hydrogen-Chlorine Actinometer.

less than a quarter of an hour in the vessel exposed to light, while the green colour of the chlorine in the other appeared to have suffered no change.

Being now no longer able, after these experiments, to doubt the influence of light in the combination of these two gases, and judging from the rapidity with which it has operated, that if the light had been much more vivid it would have operated much more quickly, we made new mixtures and . . . exposed them to the sun. Scarcely had they been exposed when they suddenly inflamed with a loud detonation, and the jars were reduced to splinters, and projected to a great distance. Fortunately, we had provided against such occurrences, and had taken precautions to secure ourselves against accident.

John Dalton also noted in June of the same year that on repeating W. Cruickshank's experiment, "the gases after being put together over water seemed to have no effect for one or two minutes, when suddenly the mixture began to diminish with rapidity," the hydrogen chloride of course was absorbed by the liquid in contact with the gas as fast as it was formed. J. W. Draper constructed an instrument—which he first called the *tithonometer* and afterwards changed the name to the *chlor-hydrogen photometer*—intended to measure the rate of combination of the two gases under the influence of light from the contraction which occurred as the hydrogen chloride which is formed is absorbed by the confining liquid. The contraction was indicated by the movement of the liquid along an index.

The tithonometer or actinometer of J. W. Draper was considerably improved by R. Bunsen and H. E. Roscoe. Fig. 5 illustrates the principles of the instrument devised by

the latter; but modified in some details. The mixture of hydrogen and chlorine from the electrolytic cell enters the tube *A*, and bubbles through the water in the flattened bulb of thin glass, *F*; the gases pass along the tube *E*, and after bubbling through the water in D, escape into the fume-chamber. The tube *B* with the 3-way cock *G* is convenient for introducing other gases into the system. The funnel-tube *C* and the cock *H* are convenient for introducing liquids into *F*. There is a ground joint at *E* useful for disconnecting the index tube *EID*; and the cock *I* is useful for arresting the liquid in *D*. With the cocks *H* closed, *G* and *I* open, the gases from the electrolytic cell are passed through the apparatus long enough to expel all the air, and saturate the liquids in the system. When all is in equilibrium, and a mixture of hydrogen and oxygen in equal volumes is slowly passing through the system, the cock *G* is closed. The position of the liquid in the index tube is noted when movement has ceased. If the bulb *F* be illuminated by the light from an oil-lamp or gas-flame, as hydrogen chloride is formed, it is absorbed by the liquid in the lower part of *F*, and the resulting contraction is measured by the left-to-right motion of the liquid in the index tube *IE*.

Starting with a mixture of hydrogen and chlorine—prepared by the electrolysis of hydrochloric acid in darkness—no movement was observed for 600 seconds after the commencement of exposure, and after that the time occupied by the liquid in moving over the 1st, 2nd, 3rd, 4th, and 5th divisions of the scale was respectively 480, 165, 130, 95, and 93 seconds, and thereafter it moved regularly at the same rate. These results are graphed in Fig. 6, as average velocities per second. Starting from the moment the mixture is illuminated by a steady source of light, there is (i) what V. H. Veley [2] afterwards called a *period of inertness*, during which there is no visible sign of chemical action; (ii) *a period of acceleration*, during which the rate of combination gradually increases to a maximum; and (iii) a *steady state* where the rate of the reaction is uniform and regular. If hydrogen and chlorine be exposed to a bright flash of light there is a momentary expansion—called the *Draper effect*, because it was first noted by J. W. Draper. This phenomenon is different from the Budde effect, for it is a secondary result of the heat liberated during the reaction; after a large number of Draper effects the amount of chemical change is measurable. It is therefore probable that there is no real period of inertness, but the amount of chemical action during the earlier stages of the reaction is too small to be detected. The initial period occupied by the reaction in assuming the steady state was called by R. Bunsen and H. E. Roscoe [3] *the period of photochemical induction*:

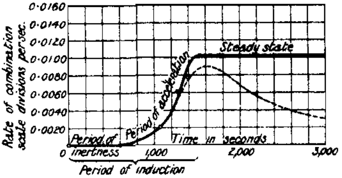

FIG. 6.—The Rate of Combination of Hydrogen and Chlorine during the Insolation of the Mixture when the product of the Reaction is removed from the system as fast as it is formed.

At one time bodies are enabled to follow the attraction of their chemical forces, whilst at another time they are prevented from doing so by forces acting in an opposite direction. These opposite attractions which must be overcome in order that the chemical combination should take place, may be presented to the mind under the image of a resistance similar to that occurring in friction, in the passage of electricity through conductors, in the distribution of magnetism in steel, or in the conduction of heat. We overcome this resistance when we quicken the formation of a precipitate by agitation, or when, by increase of temp., by catalytic action, or by insolation, we cause a chemical action to occur. . . . The act by which the resistance to combination is diminished, and the combining power thus brought into greater activity, we called *chemical induction*; and we specify this as photo-chemical, thermo-chemical, electro-chemical, and ideo-chemical, according as light, heat, electricity, or pure chemical action is the active agent concerned in overcoming the chemical resistance.

It was recognized that the initial period is characteristic of many other reactions not dependent on light, and it was called **the period of induction**. Such a period has been observed in the action of acids on zinc; of nitric acid on copper; of

sulphurous on iodic acid; of bromine on organic acids; and M. Berthelot and L. P. de St. Gilles also noticed what they called *une accélération initiale* in the action of acids on alcohol. J. W. Draper believed that the first action of light was to induce a more active allotropic modification of the chlorine; E. Pringsheim, J. W. Mellor, P. V. Bevan believed that some intermediate compound is formed in the initial stages of the reaction; but C. H. Burgess and D. L. Chapman showed that the system probably contains some impurity which must be destroyed by the light before the chlorine and hydrogen can react.

There is no general cause for the period of induction applicable to all reactions. Excluding disturbances arising from the imperfect mixing of the reacting substances, from the heat of the reaction, and from the preliminary saturation of a liquid by a gas before the speed of a reaction can be measured by the rate of evolution of a gas, etc., three causes of a period of induction have been recognized. (1) The final products of the reaction are produced after certain intermediate products have been formed. (2) The main reaction may be accelerated catalytically by the products of the reaction—*e.g.* A. V. Harcourt and W. Esson showed that the manganese sulphate produced during the reaction between potassium permanganate and oxalic acid in the presence of sulphuric acid accelerates the reaction. (3) The overcoming of a passive resistance of some kind, or the destruction of a negative or inhibitory catalyst as is supposed by C. H. Burgess and D. L. Chapman to occur when light acts on a mixture of hydrogen and chlorine containing a trace of nitrogen chloride.

A period of induction is characteristic of chemical reactions which take place in a series of intermediate stages. This is a necessary consequence of the law of mass action. The duration of the period depends on the relative magnitude of the velocity constants of the intermediate reactions. For example, with the reaction A=M=B, the rate of formation of the intermediate compound, M in the A=M reaction, will be quickest at the start, and the rate of formation of B by the destruction of M in the M=B reaction will be slowest at first, and increase with time as the amount of M accumulates in the system. At first, during the period of acceleration, the speed of the A=M reaction exerts a preponderating influence and M accumulates in the system; but the increasing speed of the M=B reaction gradually neutralizes the effect of the first reaction, until the rate of formation of M by the A=M reaction is equal to the rate of its destruction by the M=B reaction, and finally, the M is consumed faster than it is formed. The amount of M in the system at any moment thus determines the rate of formation of B, so that the curves showing (i) the rate of formation of B, and (ii) the amount of M in the system at different moments, are similar in shape. This is illustrated by the dotted line in Fig. 6. The duration of the period of induction naturally depends upon the relative speeds of the two reactions. If the rate of formation of the intermediate compound is immeasurably fast, there will be no appreciable period of induction.

In the case of the hydrogen-chlorine reaction, the intermediate compound M, by J. W. Draper's hypothesis, is allotropic or active chlorine; by E. Pringsheim's hypothesis,[4] chlorine monoxide or some analogous compound. Having shown that the additive chlorine monoxide does not accelerate the reaction or abbreviate the period of induction, an imaginary intermediate compound was postulated of a more indefinite and vague form: $xCl_2.yH_2O.zH_2$. One naturally shirks vague hypotheses of this type, but we are always confronted with the fact that the presence of the third component, water, seems necessary for this reaction. There are also many other reactions in which it seems necessary to assume either the formation of a complex intermediate compound of this type, or else a sequence of consecutive chemical reactions in which water plays an essential part. The reason for including water in the formula of the imaginary intermediate compound is to indicate that the formation of hydrogen chloride from the mixed gases, in light, seems to be dependent on its presence. In the absence of water, the dry insolated gases unite with great difficulty, if at all.

If the formation of an intermediate compound be the source of the activity of the chlorohydrogen mixture, this compound must be moderately stable in the presence of chlorine and hydrogen gases because J. W. Draper found evidence that it was not decomposed immediately the illuminated mixture of hydrogen and chlorine is darkened. He says that he kept a pre-illuminated mixture of hydrogen and chloride in darkness for ten hours, and on re-exposure to light, the movement of the liquid in the index tube commenced in a few seconds, whereas in the non-illuminated mixture 600 seconds elapsed before any movement was visible. This showed that the change which occurs in the mixture is not transient, but can persist for some hours. R. Bunsen and H E. Roscoe denied that previously insolated chlorine instantly gives rise to hydrogen chloride on exposure to light ; P. V. Bevan showed that J. W. Draper's observation is accurate, but the increased power so acquired by chlorine is lost when the gas is passed through water. Whatever is formed during the action in light is therefore either decomposed or washed out of the gas when bubbled through water R. Bunsen and H. E Roscoe's failure to verify J. W. Draper's observation was due to their having bubbled the gas through water before it was tested. If x_0 be the activity of a mixture of hydrogen and chlorine combining in light,[5] and x the activity at the time t, J. W. Mellor found that $x=x_0e^{-2t}$ for his actinometer. C. H. Burgess and D. L. Chapman noted that by shaking the actinometer with a mixture of hydrogen and chlorine, which has been insolated, the induction period on re-exposure is shorter than before, and by repetitions of this treatment, the actinometer is finally brought into such a condition that there is no period of induction on re-exposure. This makes it appear as if the liquid is sat. with the intermediate compound M. When the absorbing liquid in the actinometer is replaced by aq. soln. of salts or acids—*e.g.* barium chloride—the induction period was prolonged, this makes it appear as if the intermediate compound is not stable in the presence of certain agents.

C. H. Burgess and D. L. Chapman found the presence of ammonia—even in very small traces—makes chlorine particularly inert towards the hydrogen in light. It is assumed that the ammonia is converted into nitrogen chloride by the chlorine, and that it is nitrogen chloride which is the inhibiting agent. D. L. Chapman estimates that the presence of 10^{-6} molecular parts of nitrogen chloride makes a sensitive mixture of hydrogen and chlorine a hundred times less sensitive than when the inhibiting agent is absent. He further found that oxygen, nitric oxide, chlorine peroxide, nitrosyl chloride, nitrogen peroxide, and ozone act as inhibitors. The mixture is indifferent to the presence of carbon dioxide nitrogen, and reducing substances generally. Hence, says D. L. Chapman,

> The so-called induction period is caused by the presence in the gas of a powerful inhibitive impurity—nitrogen chloride—which must be completely removed from the gases before the chlorine and hydrogen can interact.

Further, D. L. Chapman and co-workers[6] have made the interesting and important observation that if the chlorine gas be freed from traces of certain impurities, present in the ordinary distilled water of laboratories, there is virtually no period of induction. It is assumed that an exceedingly minute trace of some impurity suffices to retard or inhibit the reaction, and that the delay in the so-called period of induction is really due to the time required to destroy this impurity before the hydrogen and chlorine gases can unite directly : $H_2+Cl_2=2HCl$. This conclusion was confirmed by M. Bodenstein and W. Dux.

Even if this interpretation be correct, the formation of hydrogen chloride by the action of light on a moist mixture of hydrogen and chlorine is possibly attended by the formation of an intermediate complex of some kind. P. V. Bevan found that when strongly illuminated chlorine is suddenly expanded, a fine rain of condensation nuclei appears when the ratio of the press. before and after expansion is 1·30 ; and a cloud appears when the expansion ratio is 1·46 ; whereas with darkened chlorine the cloud does not appear until the expansion ratio is 1·50.

Similarly, with the electrolytic mixture of hydrogen and chlorine, drops appear when the expansion ratio of the non-illuminated gas is about 1·42, and 1·22 with the illuminated gas. If the illuminated gas in which hydrogen chloride is forming *be expanded sufficiently to produce a cloud, the formation of hydrogen chloride* ceases. Hence, argues P. V. Bevan, the addition compounds of the type $Cl_2.H_2O$ are formed in illuminated chlorine, and their presence is the cause of the difference between illuminated and non-illuminated chlorine; and the formation of hydrogen chloride is due to the preliminary formation of the complex $Cl_2.H_2O.H_2$. J. W. Mellor (1902) also assumed the possible formation of the complex $xCl_2.yH_2O.zH_2$ as an intermediate stage in the reaction. M. Bodenstein and W. Dux found that the presence of water vapour with a press. between 0·004 and 2·3 mm. has no influence on the velocity, and this is said to be "adequate to rule out" the assumption that this complex is an intermediary in the reaction. A calculation of the number of water molecules per c.c. of gas represented by these press. would have shown that this is by no means the case. C. H. Burgess and D. L. Chapman (1906) conclude that the formation of condensation nuclei observed by P. V. Bevan is not essential to the production of hydrogen chloride. F. Weigert argued that the action of light is catalytic in that it is incapable of altering the equilibrium constant in the reaction $Cl_2+CO = COCl_2$ between 450° and 510°, and he assumed that the light produces complexes—*Reaktionskerne*—of some kind which act in an analogous manner to the action of the particles of platinum, in a colloidal soln. of that metal, on the decomposition of hydrogen peroxide.

Photoelectric action.—The fact that a negatively charged body rapidly loses its negative charge when exposed to ultra-violet light, while a positively charged body retains its positive charge was discovered by W. Hallwachs in 1888.[7] It was further shown that an insulated polished metal plate acquires a positive charge under similar conditions. These effects are known as the *Hallwach's effect* or the *photoelectric effect*. J. Elster and H. Geitel showed that the more electropositive the metal the greater its sensitiveness. The effect may be complicated by the nature of the surface, and by the presence of absorbed layers of gas. The alkali metals are extremely sensitive to this phenomenon, indeed, they exhibit the effect with rays of the visible spectrum—for example, the sensitiveness of three of the alkali metals for the radiations in different parts of the visible spectrum are relatively:

	Sodium.	Potassium.	Rubidium.
Blue rays	7·8	30·0	87
Yellow rays	8·2	3·5	340
Red rays	0·2	0·1	21
White light	22·0	53·0	540

According to R. Pohl and E. Pringsheim, also, the specific photoelectrical activity, or the activity for light of unit intensity increases as the wave-length diminishes. Photoelectrical activity is a constitutive property, and not an additive or an atomic property like radioactivity. Thus, the sulphides of silver, arsenic, antimony, lead, tin, and manganese are photoelectric, while sulphates of these elements are not. Dry ice is photoelectric, water is not. Fluorspar; many of the metalloids; dry hydroxides; the halides of silver and lead; zinc; aluminium; etc., show photoelectric activity in sunlight. The activity of metal surfaces usually decreases rapidly in air. The presence of neither hydrogen nor oxygen appears to be necessary for the effect. Photometers have been constructed for measuring the intensity of light in terms of the photoelectric effect by making copper oxide, or some metal like zinc, or potassium the illuminated surface.

The photoelectric effect has received its simplest explanation in terms of the electron theory in which the phenomenon is attributed to the emission of electrons under the influence of ultra-violet light. J. J. Thomson[8] proved that the carriers of negative electricity from an illuminated metal plate are identical with the cathode rays of a Crookes' tube, and consist of negatively electrified corpuscles or negative electrons carrying an electrical charge equal to that concerned in electrolytic

convection. Measurements by P. Lenard, J. Elster and H. Geitel, A. Ladenburg, and others have shown that (i) the *velocity* of the electrons discharged from an insolated metal depends only on the frequency of the incident monochromatic light; and (ii) the *number* of the electrons emitted increases proportionately with the intensity of the incident light. Assuming that the energy absorbed per mol. in any photochemical reaction is ϵ, A. Einstein[9] has shown that the quantum *theory, applied to the photoelectric effect, furnishes the relation* $\epsilon = nh\nu$, where n is an integer, h is a universal constant equal to 6.62×10^{-27}, and ν is the vibration frequency of the absorbed monochromatic radiation. This relation is called **Einstein's law of photochemical equivalence.** Hence it follows at once that the amount of photochemical action will be proportional to the intensity of the illumination.

Assuming the electronic structure of the atom, the photoelectric electrons liberated by the action of light are identified by J. Stark[10] with the valency electrons or the electrons which furnish the so-called chemical bonds. Photoelectric and photochemical changes are thus regarded as changes of the same character in that both are determined by the displacement or separation of electrons by the absorption of radiant energy. J. Stark distinguishes primary photochemical action in which *the same valency electron which has absorbed energy causes, by collision, the* separation of a valency electron from a neighbouring atom. J. Stark further postulates that primary photochemical actions (i) are unimolecular; (ii) are independent of temp.—at least for light of wave-length $450\mu\mu$; and (iii) have a velocity proportional to the amount of active light absorbed. M. Bodenstein and W. Dux[11] further postulate that the primary reaction in the case of hydrogen chloride is (iv) independent of the concentration and nature of the impurities present; and that (v) each molecule taking part in the change consumes one quantum (or a very small number of quanta) of energy. In *primary light reactions*, the molecule is ruptured by the absorbed light energy into a positive radicle and an electron, so that for every molecule so ruptured a definite quantum of energy is necessary. The positive radicle simultaneously formed is chemically active. M. Bodenstein included the decomposition of hydrogen iodide; the formation of ozone; the decomposition of ammonia; the transformation of λ- into μ-sulphur; and the decomposition of ozone by chlorine in this class. In *secondary light reactions*, electrons attach themselves to the molecules which are thereby activated so that they can take part in chemical change. In symbols: Cl_2 with light energy$=Cl_2+\ominus$, where $\ominus$ symbolizes an electron: $Cl_2+\ominus=Cl_2'$. The negatively charged molecules which have gained an electron are then capable of reacting with hydrogen: $Cl_2'+H_2=2HCl+\ominus$. After the reaction, the free electrons liberated attach themselves to other molecules, and so, acting like a catalytic agent, bring about the combination of an indefinitely large number of reacting molecules. As examples of secondary light reactions, M. Bodenstein cites the decomposition of ozone; the decomposition of oxalic acid by uranyl nitrate; the hydrolysis of hydrochloroplatinic acid; the decomposition of hydrogen peroxide; the reaction between hydrogen iodide and oxygen; the formation of phosgene; etc.

M. Bodenstein included the reaction between hydrogen and chlorine as a secondary light reaction, but gave up the hypothesis that the electrons are separated when chlorine and hydrogen react in light, because (i) the observations of J. J. Thomson, and of M. le Blanc and M. Vollmer show that there is no evidence of ionization in illuminated chlorine; and (ii) the observations of P. Lenard, and of E. B. Ludlam, show that ionization, the formation of fogs as in P. V. Bevan's experiment, and chemical action are distinct and independent results of the action of light, and are invoked by separate regions of the spectral rays. M. Bodenstein therefore assumed that the absorbed energy sets the molecules of chlorine into a state of rapid vibration when they can react with hydrogen to produce molecules of hydrogen chloride possessing a high energy content; this energy can be transferred to other molecules of chlorine—or of oxygen if that gas be present.

V. Henri and R. Wurmser[12] have measured the energy necessary for the photochemical decomposition of hydrogen peroxide, and obtained smaller values than are required by Einstein's law of photochemical equivalence for the ratio of the number of molecules which have been deprived of electrons and which react directly, to the amount of energy absorbed. E. C. C. Baly suggests that a portion of the energy in these gases is derived from the solvent; and M. Bodenstein that if the electron attached to a molecule becomes free after the secondary reaction, it is possible that smaller values for Einstein's ratio will result, because the energy required for the second separation of the electron has not been derived from the light. On the other hand, if the positive residue does not unite quickly enough with another molecule, the original molecules may be reformed, and the velocity of the reaction will be less than ought to have resulted from the absorbed energy.

According to the photoelectric hypothesis, therefore, the absorption of light is attended by the separation of electrons proportional in number to the intensity of the light per unit of illuminated surface, but independent of temp. Since on the electron theory, electrolytic dissociation and the preliminary stages of photochemical action can both be regarded as eq. to the separation of negative electrons, W. D. Bancroft has emphasized a century-old suggestion of T. von Grotthus,[13] who said:

> It is in accordance with facts as I see them to compare the chemical action of light with that of a voltaic cell. Light separates the constituents of many ponderable compounds and forces them to form new compounds . . . just as the poles of a voltaic battery do to a still greater extent.

Just as in *electrolysis* M. Faraday showed that the rate of electrochemical decomposition is proportional to the energy consumed in unit time, independently of the masses of the reacting substances, so in *photolysis*, the rate of the primary photochemical action is assumed to be proportional to the consumption, or absorption, of radiant energy in unit time, and independent of the masses of the reacting substances. Nearly all photochemical reactions which have been investigated are unimolecular, as J. Stark has assumed to be characteristic of primary photolytic changes. For instance, while the thermal decomposition of hydrogen peroxide and of hydrogen iodide follows the bimolecular law, these reactions are unimolecular when the decomposition is effected by light. M. Wildermann[14] found, on the contrary, that the reaction: $CO+Cl_2=COCl_2$, follows the bimolecular law, and states that photochemical reactions are governed by the same law of mass action as reaction in the dark; but C. H. Burgess and D. L. Chapman have properly shown that this cannot be right, since M. Wildermann has not taken into consideration the dependence of the reaction on the quality and character of the light. J. Plotnikoff found that when bromine reacts with hydrocarbons of the ethylene type, the velocity is different in light and in darkness. The equilibrium conditions agree with the assumption that the bromine reacts as 2Br and not as Br_2.

The consumption of energy during photolytic reactions.—In 1818, T. von Grotthus[15] formulated one of the most important laws of photochemistry: *Only those rays which are absorbed by a substance can produce chemical action.* This statement is usually attributed to J. W. Draper, who, in 1841, showed that the chemical action produced by the rays of light depends on the absorption of actinic energy by the sensitive body; just as an increase of temp. is produced by the absorption of heat energy. In 1843, J. W. Draper also showed that the amount of chemical action in his tithonometer is directly proportional to the time of exposure and to the quantity of incident rays. If, therefore, t be the time during which monochromatic light of intensity I be absorbed by a sensitive body, the total energy of the radiation will be kIt, where k is a constant dependent on the nature of the radiant ray. For a complex radiation, like white light, each component behaves in a similar manner, and the total energy of the radiation will be the sum of the effects produced by each, that is ΣkIt.

In a letter to J. W. Goethe in 1810, T. J. Seebeck stated that a mixture of hydrogen and chlorine gases contained in a clear glass vessel exploded in sunshine; but that under a dark blue glass, combination occurred in one minute without explosion; while under a dark red glass, the action either took place very slowly or not at all. J. E. Berard (1813) believed that the maximum effect was produced by rays in the violet part of the spectrum, and in 1841, J. W. Draper showed that the maximum effect is produced by the indigo rays, and that the effect gradually diminishes towards each end of the spectrum. It is not satisfactory to define specific parts of the spectrum by colour. R. Bunsen and H. E. Roscoe established the accuracy of the main thesis which located the more active rays for this particular reaction, about the violet end of the spectrum. According to J. M. Eder, light of every colour, from the extreme violet to the extreme red, and also the invisible infra-red and ultra-violet rays, can cause chemical action. All depends on the nature of the light sensitive medium.

Although the rays which are absorbed by a substance are alone capable of producing chemical action, the converse proposition does not obtain. Only a definite fraction of the total radiant energy absorbed by a system can do chemical work; and R. Bunsen and H. E. Roscoe inquired: What fraction of the total energy absorbed by a mixture of chlorine and hydrogen is utilized in chemical action? They found that more energy is absorbed when light passes through a mixture of equal volumes of hydrogen and chlorine than when it passes through a cylinder containing the same amount of chlorine alone. The amount absorbed by the hydrogen is immeasurably small. The amount absorbed by the chlorine, called the *optical extinction*, was supposed to be spent in raising the temp. of the chlorine; and the additional amount absorbed when the chlorine is mixed with hydrogen is spent in doing chemcial work, was called the *photochemical extinction*. Hence, they concluded:

> Of the rays from a gas-jet which are absorbed by the mixture of hydrogen and chlorine, two-thirds serve to heat the gases, while the remaining third is spent in performing the work necessary to put the two gases into such a condition that they can enter into chemical combination.

E. Pringsheim considered that it is purely an hypothesis to assume that the proportion of radiant energy which heats the gas remains the same when the gas is mixed with hydrogen and is undergoing chemical change. A larger proportion of energy may be used for activating or altering the condition of the chlorine so that it reacts to form hydrogen chloride.

C. H. Burgess and D. L. Chapman hold that

> The light absorbed by mixtures of chlorine either with hydrogen or with an inert gas such as oxygen is almost the same as it would be if the same beam of light were made to traverse the same column of chlorine from which the diluting gas has been removed. There is no indication that the light which brings about the chemical change is distinct from that absorbed by the chlorine in virtue of its optical properties. The energy which brings about the chemical change is derived from the light absorbed by the moist chlorine.

At present little more can be stated than is supplied by Stokes' dynamical theory indicated previously. The energy absorbed by chlorine is gradually dissipated as heat; and in presence of hydrogen, part of the absorbed energy confers on the gas the property of more readily combining with those substances for which it has an affinity.

Just as in Faraday's law the amount of electrolysis is proportional to the current passed through an electrolytic cell, so in Grotthus' law, the amount of photolysis is proportional to the absorbed energy of short enough wave-length to start chemical action. The departures from apparent proportionality can be explained in a similar way, the former by the phenomenon of residual currents or polarization, the latter, as shown by P. Villard, by the existence of a limiting low exposure

beyond which no sign of photolysis can be detected. M. Berthelot and H. Gaudechon, and M. Trautz say that high frequency of vibration of light is analogous to high temp. in thermal reactions, so W. R. Mott says that a high vibration frequency of light is analogous with decomposition voltage in electrolysis. The longer waves in the infra-red produce very few chemical effects, while the shorter waves in the violet and ultra-violet chemically influence an enormous number of substances. Curves of photoelectric effects with light of different wave-lengths are similar to those with different decomposition voltages. The fluorides are stable and resist the action of light more than the other halides—*e.g.* silver fluoride is not appreciably affected by light. The decomposition voltages of the halide acids, and their sensitiveness to decomposition by light of different wave-lengths, run parallel.

TABLE IV.

Acid	Decomposition voltage	Sensitiveness to light of different wave-lengths.
Hydrofluoric acid	2·2	Not decomposed by the far ultra-violet
Hydrochloric acid	1·7	Slightly decomposed by the far ultra-violet
Hydrobromic acid	1·2	Easily decomposed by the ultra-violet
Hydriodic acid	0·6	Easily decomposed by blue light

The influence of light on the three gaseous systems in quartz, uviol, and Jena glass vessels, which permitted the determination of photochemical equilibrium in three different parts of the spectrum, has been investigated from both sides of the equilibrium $X_2+H_2 \rightleftharpoons 2HX$, by A. Coehn and K. Stuckardt. The percentage decompositions of the hydrogen halides are as follows:

	Quartz glass, $\lambda > 220\mu\mu$	Uviol glass, $\lambda > 254\mu\mu$	Jena glass, $\lambda > 300\mu\mu$
Hydrogen iodide	92·2	100	100
Hydrogen bromide	100·0	c. 20	0
Hydrogen chloride	0·42	0	0

The temp. coeff. of photochemical reactions were shown by M. Padoa and C. Butironi to vary with the wave-length of the light used. Thus, with hydrogen and chlorine, the temp. coeff. of the reaction is 1·29 for white light; 1·50 for green light (530–550$\mu\mu$); 1·31 for blue light (470–490$\mu\mu$); 1·21 for violet light (440–460$\mu\mu$); and 1·17 for ultra-violet light (350–400$\mu\mu$).

According to E. Warburg,[16] the photolysis of hydrogen bromide by radiations of wave-lengths 0·209μ and 0·253μ per unit of energy absorbed increases with the wave-length, and nearly in the ratio required by Einstein's theory of photochemical action indicated above. The law can hold only when the work required in the decomposition of the molecule is smaller than the quantum of the decomposing radiation. This relation is fulfilled with hydrogen bromide with the two wave-lengths used, but is not fulfilled in the photolysis of ammonia by the wave-length 0·209μ and of oxygen by the wave-length 0·253μ. The deviations found in the last two cases are therefore explained. The mathematical theory of the reaction has been studied by J. A. Christiansen.

Active chlorine.—Consonant with J. W. Draper's observation that chlorine which has been insolated is more active chemically than chlorine which has not been exposed to light, and that the activity persists many hours, P. A. Favre and J. T. Silbermann[17] found that the heat evolved during the action of insolated chlorine on potash is greater than that of non-insolated chlorine by some 39 cals. J. W. Mellor could detect no difference by Kundt's process for the ratio of the two sp. ht. of the insolated and non-insolated gas. H. V. Vernon found that chlorine subjected to the silent discharge suffered no change in volume; nor could E. Briner and E. Durand detect a change in volume of the order of $\frac{1}{2000}$th. G. Kümmell and

F. Wobig found no difference in the relative density of illuminated and non illuminated chlorine. By leading the electrolytic gases *viâ* separate tubes into the insolation vessel of the actinometer, Fig. 5, and exposing the chlorine on its way (*a*) to acetylene light; or (*b*) to the silent discharge; or (*c*) to the heat of a Bunsen flame, J. W. Mellor (1904) found the period of induction was considerably abbreviated. M. Bodenstein and H. S. Taylor estimate that with highly purified gases, the activity induced by light does not persist longer than 6×10^{-1} sec. and that the observed activity of the insolated gas must be due to an entirely different cause.

C. Kellner (1892) patented the exposing of chlorine to the silent electrical discharge in order to make it more reactive in the preparation of bleaching powder; F. Russ (1905) also showed that chlorine activated by the silent discharge is more active in chlorinating benzene than ordinary chlorine. It is suggested that the ultra-violet rays and a certain content of moisture are necessary factors in the activation. According to S. Larsen, electrolytic chlorine is more active than ordinary chlorine, and when used for making bleaching powder, furnishes more calcium chloride and oxygen gas, but S. P. Ferchland could detect no difference, other than that due to its greater content of carbon dioxide as impurity. R. Fabinyi claims to have prepared chlorine by different processes, each of which furnished chlorine water which decomposed at different rates in light; but J. von Ferentzy showed that the results are due to the presence of different proportions of chlorine oxide, as an impurity, in the chlorine prepared by different processes.

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§ 6. The Preparation of Hydrogen Chloride and Hydrochloric Acid

One compound of hydrogen and chlorine is known with certainty. It is called **hydrogen chloride,** hydrochloric acid gas, or muriatic acid gas, and symbolized HCl. Its aq. soln. is called **hydrochloric acid,** which also is often represented by the same symbol as the gas. The names *muriatic acid* and *spirit of salt* were used by the early chemists, as indicated in connection with the history of chlorine. There is a little evidence indicating the presence of a perchloride or trichloride of hydrogen HCl_3, analogous with hydrogen tri-iodide, HI_3, in the liquid formed when chlorine is dissolved in the conc. acid. Hydrogen chloride or hydrochloric acid occurs in the emanations from fumaroles and volcanoes ; in the rivers and streams which originate in volcanic districts ; and in the gastric juices of man and other animals. Salts of the acid—the chlorides—are very abundant.

As already indicated, hydrogen chloride is formed by the direct union of the elements. The two gases do not combine in darkness ; H. Gautier and H. Hélier[1] kept the mixed gases between 15 and 16 months in darkness without sign of combination ; in daylight the gases gradually unite, and this the more rapidly the more intense the illumination, until, in sunlight, the mixture explodes. Similar remarks apply when the mixed gases are illuminated by artificial light—with the light from a candle, gas or oil flame, the gases combine comparatively slowly ; but when illuminated by more intense light—*e.g.* the lime-light, magnesium flash-lamp—the mixture may combine explosively. J. W. Mellor and E. J. Russell found that if the gases are well dried, no explosion occurs in sunlight, and about 30 per cent. combined after three days' exposure to June's sunshine.

Hydrogen burns in chlorine, and chlorine burns in hydrogen. According to C. Fredenhagen and C. Killing, the temp. of the chlorohydrogen flame is a little higher than Bunsen's flame. According to C. Killing, the hydrogen flame on a Welsbach mantle in chlorine gives a bright green light. The mixture of gases—moist or dry—explodes when ignited by an electric spark. According to H. B. Dixon, the explosion wave travels at the rate of 1745 metres per second in the electrolytic mixture of hydrogen and chlorine dried by conc. sulphuric acid, and nearly 1¼ per cent. slower, or 1729 metres per second, in the moist gas. With an excess of hydrogen, the rate is faster, being 1849 metres per second in the mixture $2H_2+Cl_2$; and 1855 metres per second in the mixture $3H_2+Cl_2$.

According to F. Freyer and V. Meyer, the gases are ignited if they be heated in a

closed vessel between 170° and 240° ; or if a stream of the gas be heated between 430° and 440°. The ignition temp. depends so much on the conditions under which the gases are heated that very variable numbers have been reported. J. W. Mellor and E. J. Russell found no explosion occurred with bulbs of the dried gases at 450°, whereas the moist gases exploded at 260°. According to J. L. Gay Lussac and L. J. Thénard, the mixed gases can be exploded by a piece of brick at 150°, while platinum black (S. Cooke), or charcoal (J. F. L. Meslens), may produce an explosion at ordinary temp. in the dark ; in any case, they start the gases reacting—presumably by catalysis. According to P. Mathieu, when a mixture of hydrogen and chlorine is exposed to the spark of an induction coil, explosion occurs only when the mixture has between 8·1 and 85·7 per cent. of hydrogen ; while when exposed to the radiation from the magnesium flame, the limits are 9·8 and 52·5 per cent. of hydrogen. The difference is attributed to the good conductivity of hydrogen for heat.

E. J. A. Gautier and H. Hélier [2] found that in light, the rate of the reaction was augmented by increasing the proportion of chlorine beyond that required for the reaction : $H_2+Cl_2=2HCl$; similarly also with hydrogen, but the effects were less pronounced than with the hydrogen. In agreement with M. Berthelot's suggestion, the results were presumably disturbed by the walls of the containing vessel. R. Bunsen and H. E. Roscoe showed that the presence of oxygen as an impurity retards both the period of induction and the rate of combination ; and, according to D. L. Chapman, for small quantities of oxygen as an impurity, the velocity of the photochemical reaction is decreased proportionally with the increase in the amount of oxygen. According to R. Luther and E. Goldberg, the photo-chlorination of hydrocarbons is inhibited by oxygen, and E. Goldberg suggests that oxygen acts as a specific poison to chlorine in photolytic changes. The desensitizing action of oxygen has also been noted in other photolytic reactions—*e.g.* mercuric chloride and oxalic acid ; the silver halides ; etc. In M. Bodenstein's first hypothesis, the retarding effect of oxygen is explained by assuming the electrons are partially consumed in activating the oxygen to form ozone which in turn re-forms oxygen ; in his second hypothesis, the newly formed molecules of hydrogen chloride communicate part of their vibratory energy to oxygen molecules instead of to the reacting gases. Instead of using R. Bunsen and H. E. Roscoe's actinometer, M. Bodenstein and W. Dux exposed bulbs of the mixed gases to light for a definite period, and solidified the hydrogen chloride and the residual chlorine by cooling with liquid air. The partial press. of the unused hydrogen was then determined. They thus established the facts : The reaction is of the second order, and is proportional to the square of the chlorine concentration ; while the concentration of the hydrogen is without influence if not less than one-fourth the volume of the chlorine be present. With smaller concentrations of hydrogen, the volume decreases slightly. The hydrogen chloride formed in the reaction has no influence on the speed of the reaction. Oxygen retards the reaction in such a way that the velocity of all stages of the combination is inversely proportional to the oxygen concentration. If I represents the quantity of light absorbed in the reaction ; t the time ; and if concentrations be represented by symbols in square brackets,

$$\frac{d[2HCl]}{dt}=kI\frac{[Cl]^2}{[O_2]}$$

R. Bunsen and H. E. Roscoe's observation that an excess of hydrogen lowers the sensitiveness of an electrolytic mixture of hydrogen and chlorine is regarded as an erroneous result caused by the contamination of the hydrogen with oxygen. Unlike M. Bodenstein and W. Dux, D. L. Chapman and L. K. Underhill found that "as the partial press. of the hydrogen is increased from zero, the rate of formation of hydrogen chloride per unit volume of the mixture is at first almost proportional to the concentration of the hydrogen, but the ratio of partial press. of hydrogen to

velocity of interaction rises continuously in value as the proportion of hydrogen is increased, and when the press. of hydrogen has attained a definite value, the rate of formation of hydrogen chloride becomes a maximum, and then, as the proportion of hydrogen is still further increased, the rate of interaction of chlorine and hydrogen falls very slowly." D. L. Chapman and J. R. H. Whiston also find that their results agree with a fairly close approximation to

$$\frac{d[2HCl]}{dt}=kI\frac{[Cl_2]}{[O_2]}$$

that is, assuming that the term $I[Cl_2]$ is proportional to the radiation absorbed per second, the rate of formation of hydrogen chloride is proportional to the radiation absorbed, and inversely as the concentration of the oxygen. D. L. Chapman and J. R. H. Whiston also found that with moist gases the amount of hydrogen chloride formed in unit time is almost independent of the press., which would not be the case if M. Bodenstein and W. Dux's formula were accurate.

H. Sirk heated mixtures of hydrogen with from 3·5 to 81·6 per cent. of chlorine for 60 minutes at 242·5°, in darkness, and then measured the amount of combination. With the mixture containing 3·5 per cent. of chlorine, 0·5 per cent. of gas was converted into hydrogen chloride; with the mixture with 51·5 per cent. of chlorine, 8·6 per cent. into hydrogen chloride, and with the mixture with 81·6 per cent. of chlorine, 12·0 per cent. was converted into hydrogen chloride. The reaction is neither bimolecular nor unimolecular. The initial velocity is approximately that required for a unimolecular reaction, being proportional to the concentration of the chlorine and independent of that of the hydrogen chloride or hydrogen. In that case $k=\frac{1}{60}\log\{a/(a-x)\}$, where a denotes the percentage amount of chlorine initially present; x, that of hydrogen chloride; and k is the affinity constant approximately 0·0012. K. H. A. Melander found the reaction between 205° and 255° to be bimolecular. The temp. coeff. of the reaction studied by E. J. A. Gautier and H. Hélier, was approximately eq. to an increase of 1·6 for a rise of 10°. K. H. A. Melander found the temp. coeff. of the bimolecular reaction $H_2+Cl_2=2HCl$ between 205° and 255° to be 2·01, and he noted that the presence of sulphur dioxide or sulphuric acid, accelerated the reaction to a marked extent. It is assumed that sulphuryl chloride is formed as an intermediate compound. P. V. Bevan found the temp. coeff. for white light to be 1·21 for 10°.

W. P. Jorissen and W. E. Ringer [3] found a slight formation of hydrogen chloride after exposing for 33 hrs. a mixture of hydrogen and chlorine to those rays from radium which will penetrate thin layers of glass. H. S. Taylor found the reaction velocity of hydrogen and chlorine under the influence of α-radiations to follow the unimolecular law. The difference in the order of the reaction under the influence of light, and of the α-radiations, is attributed to the relatively larger amount of energy absorbed from incident light by the chlorine. J. J. Thomson found the rate of combination of an insulated mixture of hydrogen and chlorine was not affected by exposure to X-rays, thorium radiations, etc. M. le Blanc and M. Vollmer found that 0·03 c.c. of hydrogen chloride was formed during 50 secs.' exposure of a mixture of hydrogen and chlorine to the X-rays. It is estimated that a single electron can bring 10^4 molecules into reaction. A. de Hemptinne found a mixture of hydrogen and chlorine at the moment of explosion is electrically conducting; but M. Trautz and F. A. Henglein found no evidence of ionization during the reaction between chlorine and hydrogen, nor between chlorine and hydrogen bromide: $2HBr+Cl_2 \rightleftharpoons Br_2+2HCl$.

Hydrogen chloride is produced in numerous reactions such as when chlorine acts on various hydrogen compounds of the metals or the non-metals. Chlorine does not attack hydrogen fluoride, but it does attack hydrogen sulphide, hydrogen iodide, ammonia, phosphine, arsine, boron hydride, water, etc., with the formation of hydrogen chloride. In many cases the action occurs at ordinary temp. Deacon's process for chlorine is based on the oxidation of hydrogen chloride by oxygen; but as

already shown, the reaction is reversible, and chlorine attacks steam forming hydrogen chloride and oxygen. Water is not decomposed by chlorine in darkness, but is slowly decomposed in daylight, more rapidly in sunlight. Steam is decomposed when it is mixed with chlorine and passed through a red-hot tube—oxygen and hydrogen chloride are the products of the reaction. This reversal of the Deacon process takes place much more rapidly if an oxidizable substance is present capable of removing the free oxygen from the system as fast as it is formed. According to R. Lorenz,[4] and H. D. Gibbs, if the tube contains carbon, the reaction is symbolized: $C+H_2O+Cl_2=CO+2HCl$; but A. Naumann and F. G. Mudford state the primary reaction is $2Cl_2+2H_2O+C=4HCl+CO_2$; and the carbon monoxide present in the gas is a secondary effect of the reduction of the carbon dioxide by the excess of carbon, as is evidenced by the greater yield of carbon monoxide if the column of carbon is made longer, or if the gases are passed through the tube more slowly. Some carbon monoxide may be oxidized by the chlorine and steam: $Cl_2+H_2O+CO=CO_2+2HCl$. If steam be in excess, some hydrogen is formed, and this the more the higher the temp. or the longer the gases are in contact with the hot carbon. When many organic compounds are treated with chlorine, part of the hydrogen is evolved as hydrogen chloride—*e.g.* with turpentine, $C_{10}H_{16}$, at ordinary temp.: $C_{10}H_{16}+8C=10CCl_2+16HCl$; and hydrogen chloride is a by-product in the preparation of chlorinated organic compounds—*e.g.* chlorobenzene, chloro-acetic acid, etc. A. Mitscherlich says that all organic compounds are decomposed by chlorine at a red heat—the hydrogen forms hydrogen chloride, and if oxygen be present, part or the whole of the carbon is oxidized to carbon monoxide or dioxide.

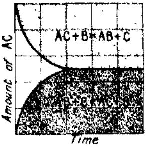

FIG. 7.—Balanced Reaction: $AB+C\rightleftharpoons AC+B$.

Several chlorides are reduced by heating them with hydrogen—*e.g.* many chlorides of the heavy metals—$2AgCl+H_2=2Ag+2HCl$; and, according to W. Spring,[5] even the alkali chlorides are reduced by hydrogen at a red heat. A. Jouniaux has reported a curious phenomenon in connection with the reduction of silver chloride or bromide by hydrogen. In the reaction $AB+C\rightleftharpoons AC+B$, the idea that at any assigned temp. the composition of the equilibrium mixture is the same no matter whether this state be approached from the left side, $AB+C$, or from the right side, $AC+B$, of the equation, is illustrated by Fig. 7. The balancing of such a reaction, however, does not always furnish the same equilibrium mixture when it is approached from different sides. Thus, A. Jouniaux (1901)[6] found that in the reaction $2AgCl+H_2=2HCl+2Ag$ the reduction of silver chloride by hydrogen stops before the system has attained the same condition as is obtained when hydrogen chloride reacts with silver. The curves, Fig. 7, are plotted from the experimental data obtained, starting with tubes *A*, containing silver chloride and hydrogen, and tubes, *B*, containing hydrogen chloride and silver—at 448°.

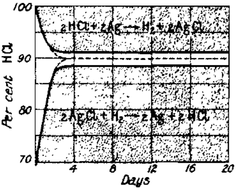

FIG. 8.—False Equilibrium.

Time heated	7–8	24	36	70	408	504 hrs.
Per cent. HCl (*A*)	71·1	81·6	82·5	88·7*	88·8	88·4
Per cent. HCl (*B*)	96·0	93·9	92·9	91·5*	91·6	91·5

The numbers succeeding the asterisk show that equilibrium was in all probability then attained. The dotted curve, Fig. 8, shows the probable state which would occur if the reactions balanced as in the ideal state indicated in Fig. 7. Indeed, if the temp. exceeds 490°, the final state is the same whatever be the initial products. The space between the two lines represents a system below 490° in what P. Duhem calls *un état de faux équilibre*. The region where there is no reaction and where

the state of **false equilibrium** occurs, is not stippled in the diagram. Several other examples of the phenomenon have been recorded. H. Pélabon has reported a similar phenomenon in connection with the reduction of silver sulphide by hydrogen, and in the action of hydrogen on sulphur or selenium. R. Engel (1885) stated that the equilibrium in the reaction $MgCO_3.3H_2O + KHCO_3 + nH_2O \rightleftharpoons MgCO_3.KHCO_3.4H_2O + (n-1)H_2O$ is not the same when approached from different sides. E. H. Büchner (1908) found that if the reaction is allowed to progress 32 days instead of a few hours the same final condition is attained from whichever side equilibrium is attained. There are reasons for the suspicion that the mixture was assumed to be in equilibrium when it was really not so;[7] and that there are no experimental grounds for the theory of false equilibrium unless some complication is involved such as was observed by H. Pélabon in the case of bismuth and hydrogen sulphide, where the formation of a film of bismuth sulphide protected the metal from the further action of the hydrogen sulphide.

The source of most of the hydrogen chloride manufactured on a large or small scale is one of the common chlorides. In the laboratory the gas is usually prepared by heating a mixture of sulphuric acid and sodium chloride; the gas can be dried by calcium chloride or conc. sulphuric acid, Fig. 9, and collected over mercury, or by the upward displacement of air. Conc. sulphuric acid acts vigorously at ordinary temp. forming a very viscid mixture when warmed; if the acid be diluted with one-sixth to one-fourth its weight of water, the gas comes off at ordinary temp., and the mixture froths a little when warmed; with equal parts of acid and water very little gas is given off at ordinary temp., but a copious quantity is given off when the mixture is warmed. If 100 parts of sodium chloride and about 170 parts of conc. sulphuric acid be used, the sodium chloride is all decomposed on the application of a gentle heat, and the residue is easily emptied from the flask. With a larger proportion of sodium chloride the reaction is not complete. The turbulence of the reaction can be lessened by using fragments of rock salt.[8]

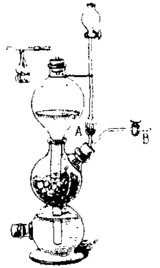

Fig. 9.—H. Erdmann's Apparatus for Hydrogen Chloride.

The reaction seems to occur in two stages. In the one stage at the lower temp. sodium hydrogen sulphide, $NaHSO_4$, is formed, $NaCl + H_2SO_4 = NaHSO_4 + HCl + 0.8$ Cals. According to C. W. Volney,[9] when a mol. each of sodium chloride and sulphuric acid (sp. gr. 1·84) are treated at 18°, the reaction is symbolized $2NaCl + 2H_2SO_4 = NaHSO_4.H_2SO_4 + HCl + NaCl$; and when the mixture is heated to 120°, there is a further evolution of hydrogen chloride; $NaHSO_4.H_2SO_4 + NaCl = 2NaHSO_4 + HCl$. In the next stage, sodium sulphate, Na_2SO_4, is formed at about 500°, $NaCl + NaHSO_4 = Na_2SO_4 + HCl + 15$ Cals, or $2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl + 15.8$ Cals. G. Neumann recommended treating carnallite with conc. sulphuric acid in a similar manner. The same gas is sometimes made in the laboratory by dropping conc. sulphuric acid into conc. fuming hydrochloric acid containing sodium chloride or ammonium chloride. L. L. de Koninck[10] decomposed ammonium chloride by dropping conc. sulphuric acid directly on solid ammonium chloride.

H. Erdmann's apparatus for preparing hydrogen chloride in a Kipp's apparatus is illustrated in Fig. 9. The middle bulb of the Kipp's apparatus contains pumice stone; the upper and lower bulbs contain hydrochloric acid; the upper end of Kipp's apparatus is closed by a rubber stopper fitted with a bulb containing potash lye. The separating funnel contains conc. sulphuric acid, and it leads to the inner bulb *viâ* a trap *A* containing sufficient mercury to cover the opening of the down-tube from the separatory funnel. Otherwise the diagram explains itself. A wash-bottle can be fitted to the exit tube *B* in the ordinary way.

In the manufacture of salt cake, about half a ton of salt, in a cast-iron pan built in brickwork, is treated with sulphuric acid (sp. gr. 1·7); torrents of hydrogen

chloride escape through a flue in the dome of the brickwork. When about 70 per cent. of the hydrogen chloride has escaped: $NaCl+H_2SO_4=NaHSO_4+HCl$, the mixture is raked into another part of the furnace, where it is heated to redness. The remainder of the hydrochloric acid escapes *via* another flue: $NaHSO_4+NaCl=Na_2SO_4+HCl$. In Hargreaves' process, a mixture of sulphur dioxide, air, and steam is passed over salt heated to about 530°. The reaction is represented: $4NaCl+2SO_2+O_2+2H_2O=2Na_2SO_4+4HCl$. The hydrogen chloride evolved in either of these processes is absorbed by water. In the early days of the Leblanc salt-cake process, the hydrochloric acid was allowed to escape into the air; as the use of the process extended, serious damage was caused by the escaping fumes; and manufacturers were compelled to consider the advisability of condensing the acid. In 1836, W. Gossage[11] adapted Gay Lussac's coke tower for the purpose, but even then a considerable amount of acid escaped. By the Alkali Act of 1863 manufacturers were compelled to adopt an efficient means of condensing the acid, for they were not permitted to allow more than 5 per cent. to escape into the air; and by the Act of 1874 this amount was reduced to 0·2 gram of HCl per cub. ft. of gas. The problem of condensation not only involves the removal of the acid from the flue gases so as to satisfy the requirement of these regulations, but it also involves the condensation of the acid in such a form that only saleable conc. hydrochloric acid is produced. The results now attained are so good that between 99·25 and 99·5 per cent. of the gas in question is recovered in the form of hydrochloric acid of sp. gr. 1·17. The best conditions for the condensation require to be adapted to (i) the temp.; (ii) the concentration of the hydrogen chloride in the flue gases; and (iii) the time the gases are in contact with the absorbent water. The hot gases are cooled by passage through tanks or batteries of tubes, or stoneware Woulffe's bottles with a counterflow of water, and subsequently passed up large towers filled with coke, or earthenware balls or discs. A spray of water descends from the top of the tower and meets the gases rising upwards from the base. It is said that R. Cellarius' receiver, Fig. 10, gives satisfactory results. Water flows in at *A*, then over the saddle, and out at *B*; the gas enters at *C* and escapes at *D*. A large surface of water is thus exposed to the gas. The vessels can be kept cool by immersion in tanks of water.

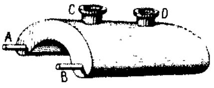

Fig. 10.—R. Cellarius' Receiver.

Water decomposes several chlorides of the non-metals, but not carbon tetrachloride. Water decomposes the chlorides of aluminium, and tin at ordinary temp.; lead chloride is decomposed by steam at 110°, and even the alkali chlorides, according to W. Spring,[12] are decomposed by steam at temp. exceeding 500°, and W. Mills proposed to obtain hydrogen industrially by heating sodium chloride with water gas. With sodium chloride, the thermal value of the reaction with steam is: $2NaCl+2H_2O=2NaOH+2HCl-61·6$ Cals.; with magnesium chloride: $MgCl_2+H_2O=MgO+2HCl-21·0$ Cals.; and with calcium chloride, similarly, $-52·0$ Cals. are required. Hence, less energy is probably required to form hydrogen chloride by the action of steam on magnesium chloride than is the case with sodium or calcium chloride. As a rule, a highly endothermic reaction usually requires prolonged furnace operations which are costly in labour, fuel, and refractory linings for the furnaces.

Instead of decomposing sodium chloride with sulphuric acid in order to obtain sodium sulphate, attempts have been made to prepare hydrogen chloride from sodium chloride, leaving a by-product of greater commercial value than sodium sulphate. Some of these processes furnish chlorine—*q.v.* Most of the proposals have either not been applied at all on an industrial scale, or else have had a very brief industrial life. For example, it has been proposed to heat an intimate mixture of *sodium chloride* and clay with steam, and to obtain sodium silicate and hydrogen chloride as products of the main reaction. A. Gorgeu[13] has shown that clay with about 35 per

cent. of alumina decomposes about 22 per cent. of its weight of sodium chloride at about 550°. The proposal failed on account of the cost of the wear and tear of the apparatus. The Daguin Co. treated a mixture of manganous and sodium chlorides with air containing about 10 per cent. of sulphur dioxide ; the final products were sodium sulphate, and hydrogen chloride—the manganous chloride acted catalytically through the intermediate formation of manganese sulphate. J. Townsend used a mixture of magnesium sulphate and sodium chloride.

Similar proposals have been made to treat the enormous quantities of *calcium chloride* obtained as a by-product in many industries either to obtain chlorine (*q.v.*) or hydrogen chloride. J. T. Pelouze [14] showed that when calcium chloride is mixed with sand to prevent fusion, it is readily decomposed by steam at a red heat with the copious evolution of hydrogen chloride, and the reaction was the basis of the E. Solvay patents in which the calcium chloride was mixed with sand or clay. W. Bramley mixed the calcium chloride with iron ore before heating it in a stream of air for chlorine, or with steam for hydrogen chloride. W. H. Seamon proposed to treat molten calcium chloride with acetylene to produce calcium carbide and hydrogen chloride.

The consumption of energy in the decomposition of magnesium chloride is much less than with sodium, or calcium chlorides. H. Davy knew that *magnesium chloride* is decomposed when heated. Even on evaporating an aq. soln. of magnesium chloride, hydrochloric acid is given off when the ratio $H_2O : MgCl_2$ is less than 6 : 1 ; and, with further evaporation, the decomposition is so great that it was once believed the reaction: $MgCl_2+H_2O=MgO+2HCl$, is complete. According to G. Eschellmann, when the hydrated salt, $MgCl_2.6H_2O$, is heated by itself to 250°, one-third of the chlorine is lost as hydrogen chloride, and the residue contains the eq. of $2MgO+4MgCl_2+3H_2O$. No further change occurs if the temp. is raised to 350°, but at higher temp. more hydrogen chloride is lost until, at 550°, about half the chlorine is lost, and a white crystalline oxychloride $MgO.MgCl_2$ remains. This oxychloride is soluble in water with the evolution of much heat. Similar results are obtained if the salt be heated in a stream of inert gas.

The magnesium chloride in the mother-liquors of sea-water, and the waste products in the manufacture of potassium salts at Stassfurt, have attracted much attention. It is estimated that in the latter case there is sufficient magnesium chloride to give enough chlorine and hydrogen chloride to satisfy the requirements of the whole world. G. Eschellmann, and B. Kosmann [15] have studied the processes for the utilization of magnesium chloride in the manufacture of chlorine and hydrochloric acid. The different proposals to manufacture hydrogen chloride from magnesium chloride have been classified as : (i) Processes in which the magnesium chloride is heated in a current of steam. The heating is done externally in suitable boilers ; [16] (ii) Processes in which the magnesium chloride is heated with substances which lose their water of crystallization at a high temp.—*e.g.* magnesium sulphate, calcium chloride, damp sawdust: [17] (iii) Processes in which the magnesium chloride alone or mixed with some other substances is heated in steam, directly by a flame.[18]

Some proposals have been made for treating ammonium chloride obtained by crystallization from the mother-liquor in E. Solvay's process. L. Mond (1883) [19] patented the heating of the ammonium chloride with sulphuric acid to 120°, and converting the ammonium bisulphate so formed with ammonia vapour to produce the normal sulphate. Later, L. Mond (1886) conveyed the vapour of ammonium chloride over oxides of cobalt, nickel, iron, manganese, aluminium, copper, or magnesium, which retain the hydrogen chloride. F. Gilloteaux proposed heating the ammonium chloride with sodium or ammonium bisulphate whereby hydrogen chloride is evolved, and the normal sulphate: $2NaHSO_4+2NH_4Cl=2HCl+(NH_4)_2SO_4+Na_2.SO_4$. When the normal sulphate is heated ammonia is given off and the bisulphate reformed: $(NH_4)_2SO_4+Na_2SO_4=2NH_3+2NaHSO_4$. The first-named reaction is not complete, and L. Mond considers that there is no reaction

between ammonium chloride and bisulphate. If the temp. is high enough, the bisulphate alone sublimes. O. N. Witt proposed treating the ammonium chloride with syrupy *phosphoric acid*; hydrogen chloride and ammonium phosphate are formed, and when the latter is heated further, ammonia and vitreous phosphoric acid are formed. There is a difficulty in finding materials to resist the corrosive action of the phosphoric acid, and only 63·6 to 86·1 per cent. of the ammonia is recovered.

Impurities in hydrochloric acid.—The chief impurities found in commercial hydrochloric acid are (i) *Sulphurous acid* produced by the action of the sulphuric acid on the iron, or on organic matter. (ii) *Sulphuric acid* derived from the acid used in decomposing the salt; in bad cases over 2 per cent. may be present. (iii) *Free chlorine* derived from the action of oxidizing agents on the hydrogen chloride. (iv) *Ferric chloride* derived from the iron vessels with which the acids come in contact. (v) *Arsenic* largely derived from the pyrites used in making the sulphuric acid. The arsenic forms arsenic trichloride, and in that form gets to the condensing apparatus. (vi) *Selenium* compounds have been found in hydrochloric acid by W. Crookes, and, according to W. B. Hart,[20] this is the cause of the yellow colour of the acid; T. Bayley says the yellow colour is due to organic matter; and others have attributed it to ferric chloride. (vii) *Bromine* has been reported by W. Crookes and G. C. Wittstein; (viii) *hydrofluoric acid* by J. Nicklès; (ix) *iodine* (x) and *thallium* by W. Crookes; and (xi) *copper* by L. R. W. McCay.

Purification of hydrochloric acid.—When pure hydrochloric acid is required, it is usually best to prepare it with pure materials rather than attempt to purify the impure acid; and the commercially pure acid is usually satisfactorily pure. T. W. Richards and R. C. Wells[21] found it sufficient to treat the purest acid of commerce with a few crystals of potassium permanganate. The soln. was diluted and boiled so as to expel bromine and iodine, and oxidize any trace of organic matter which might be present. The soln. was fractionally distilled and the middle fraction selected for use. C. Wigg removes sulphuric acid by barium or strontium chloride; and sulphur dioxide by manganese dioxide. F. Haber and S. Grinberg remove chlorine by treatment with mercury. O. Bettendorf removed arsenic by treating the acid with stannous chloride and distilling the filtrate. If the acid be weaker than a sp. gr. 1·123, the precipitation will be incomplete; and no precipitation occurs if the acid has a sp. gr. 1·100—because, it is said, the arsenic is then present as As_2O_3 instead of as $AsCl_3$. According to H. Hager, the product always contains some arsenic if the precipitate is not completely filtered off before distillation: $3SnCl_2+As_2O_3+6HCl=2As+3H_2O+3SnCl_4$. I. Mayrhofer has shown that mere oxidation of the arsenic chloride to arsenic acid and subsequent distillation is not effective, for the arsenic acid is decomposed by hydrochloric acid, especially on heating, forming arsenic trichloride, and this the more the greater the concentration of the acid. Hence proposals—by H. Rose, R. Otto, E. Bensemann, A. Houzeau, H. B. Bishop, etc.—to oxidize the arsenic with potassium chlorate and then distil the acid, cannot be effective. T. Diez and R. Otto treated the acid with hydrogen sulphide, and distilled the filtered product; R. Engel used sodium thiosulphate; J. W. Leather, barium sulphide; M. N. d'Andria, precipitated zinc sulphide; and L. Ducher, sodium sulphide. H. Beckhurts distilled the acid from ferrous chloride rejecting the first 30 per cent. of the distillate. L. T. Thorne and E. H. Jeffers claim to make arsenic-free acid by diluting the acid to be purified to a sp. gr. 1·10, and adding a piece of previously feebly calcined copper gauze to the boiling acid. After boiling an hour, remove the old copper gauze and add a fresh piece The arsenic is precipitated on the copper. The treatment is repeated until the copper remains quite clean when boiled for an hour in the acid. The acid is distilled from a clean piece of copper gauze in order to prevent the ferrous chloride oxidizing to the volatile ferric chloride.

Hydrochloric acid is comparatively cheap because it is produced in great abundance as a by-product in the manufacture of salt-cake. It cannot be stored in lead

or iron vessels because these metals are attacked ; it is usually stored in large glass balloons or large stoneware vessels.

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§ 7. The Preparation of Hydrogen Bromide and Hydrobromic Acid

It is convenient to call the gas *hydrogen bromide*, and a soln. of the gas in water *hydrobromic acid*. If a 48 per cent. soln. of hydrobromic acid is warmed with anhydrous calcium bromide, or if conc. hydrobromic acid is treated with phosphorus pentoxide, hydrogen bromide is obtained.[1] Hydrogen does not unite with bromine or iodine at ordinary temp. even when exposed to sunlight. At 196°, however, J. H. Kastle and W. A. Beatty[2] found that bromine and hydrogen unite completely in sunlight, but not in darkness; the amount of combination is approximately proportional to the time of exposure. At 100°, there is a slight formation of hydrogen bromide in sunlight. M. Bodenstein and S. C. Lind measured the velocity of the reaction under the influence of heat, and they did not find the reaction followed the bimolecular law. Hydrogen bromide retards the reaction more than corresponds with its presence as a product of the reaction. Iodine exerts a similar retarding influence. J. A. Christiansen explains M. Bodenstein and S. C. Lind's results by assuming the formation of hydrogen bromide proceeds with the primary reaction: $Br+H_2 \rightleftharpoons HBr+H$, attended by $H+Br_2 \rightleftharpoons HBr+Br$, and he calculates for the thermal value, $Br+HBr \rightleftharpoons Br_2+H+43.7$ Cals.

If a stream of hydrogen be bubbled through warm bromine, the hydrogen which passes along is highly charged with bromine vapour, and when ignited, dense clouds of hydrogen bromide are formed. A. J. Balard[3] showed that if a mixture of hydrogen and bromine vapour be passed through a red-hot tube containing iron turnings hydrogen bromide is formed, and B. Corenwinder obtained a rapid combination by passing the elements over heated platinized asbestos, or a hot platinum spiral. The platinum acts as a stimulant or catalytic agent.

G. P. Baxter and F. B. Coffin[4] used this process for preparing hydrobromic acid for their work on at. wt. The hydrobromic acid was condensed in water contained in a cooled flask. In order to remove iodine, the soln. was diluted with water, and twice boiled with a little free bromine. A small quantity of potassium permanganate added, and the bromine set free was expelled by boiling. The acid was finally distilled with the aid of a quartz condenser, and the first third rejected.

According to A. J. Balard,[5] hydrogen bromide is not formed by passing a mixture of water vapour and bromine through a red-hot tube, but J. Bourson did get a mixture of oxygen and hydrogen bromide under these conditions at a high temp.,

and C. Löwig found that bromine water in sunlight decomposes like chlorine water, but with greater difficulty. A. J. Balard also noted in his historic memoir that bromine water with reducing agents—*e.g.* hypophosphorous acid, sulphur dioxide, arsenic trioxide, hydrogen sulphide, hydriodic acid, and aq. ammonia—form hydrogen bromide. T. Curtius and H. Schulz found that hydrazine hydrate with an excess of bromine gives nitrogen and hydrogen bromide; and A. Connell that boiling bromine with fuming nitric acid furnishes some hydrogen bromide. J. H. Gladstone reduced bromine with sodium thiosulphate; H. Pickles, with stannous chloride; C. Méne, with crystallized sodium sulphite and with calcium hypophosphite; and E. Leger, with sulphur dioxide; and P. Hautefeuille, with hydrogen iodide. A. Scott recommends passing a rapid current of sulphur dioxide through a mixture of 350 grms. of bromine and two litres of water, until a pale yellow homogeneous liquid is formed. This is then distilled in a gentle current of air until the residual liquid has a sp. gr. of about 1·7. The distillate is then re-distilled, rejecting the first fraction. The distillate is again redistilled from a little barium bromide to retain the sulphuric acid. It is claimed that, in the ordinary methods of preparation with phosphorus, the arsenic in the phosphorus forms arsenic bromide which contaminates the product.

The bromides of phosphorus, sulphur, selenium, arsenic, and similar compounds furnish hydrogen bromide when treated with water—*e.g.* $PBr_3+3H_2O=H_3PO_3+3HBr$. Hydrogen bromide is also obtained by the joint action of bromine, water, and phosphorus.[6]

The following is a method commonly employed in the laboratory: Mix, say, 10 grms. of red phosphorus with 80 grms. of fine sand, and place the dry mixture in a dry distillation flask, *A*, Fig. 11. Add about 20 c.c. of water. Close the flask with a rubber stopper fitted with a tap funnel *B*, and delivery tube as indicated in the diagram. The end of the tap funnel is drawn to a fine point. Connect the delivery tube with a tower or a U-tube *C* containing glass wool and slightly damp red phosphorus. The gas may be collected by the upward displacement of air, or absorbed in water as illustrated in the previous diagram; or collected over mercury, *E*. In the latter case, a safety funnel may be attached to the delivery tube at *D*, so that variations of press. inside the apparatus may be rapidly adjusted without risk of explosion and back suction of mercury. About 60 grms. of bromine are placed in the tap funnel, and allowed to fall, drop by drop, on the red phosphorus. As each drop of bromine comes in contact with the phosphorus, a flash of light is produced. Some prefer to keep the flask immersed in cold water during the early stages of the reaction, and to wrap a towel round the flask in case of an explosion. The heat of the reaction volatilizes some bromine which is retained by the phosphorus in the U-tube; when all the bromine has been run into the flask, a further quantity of hydrogen bromide may be obtained by gently warming the flask. The hydrogen bromide can be dried by means of a tube packed with calcium bromide.

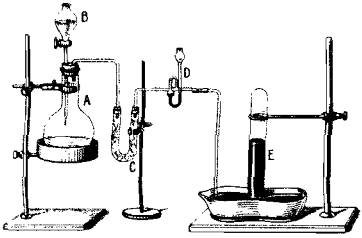

FIG. 11.—Preparation of Hydrogen Bromide.

The chemical reactions which occur during the preparation of hydrogen bromide by the action of bromine on phosphorus and water, are probably somewhat as follows: Phosphorus tri- and penta-bromide are first formed; these react with the water; $PBr_3+3H_2O=H_3PO_3+3HBr$; and: $PBr_5+4H_2O=H_3PO_4+5HBr$. The whole reaction is usually represented on the supposition that phosphorus tri-bromide is formed: $2P+6H_2O+3Br_2=2H_3PO_3+6HBr$. If too little water be present, some crystals of phosphonium bromide—PH_4Br—may be formed in the flask owing to the decomposition of the hot phosphorous acid, H_3PO_3, as represented in symbols: $4H_3PO_3=3H_3PO_4+PH_3$; and $PH_3+HBr=PH_4Br$.

Hydrogen bromide is formed when bromine acts on hydrogen sulphide,[7] and hydrobromic acid is formed when hydrogen sulphide is passed into bromine covered with a layer of water: $H_2S+Br_2\rightleftharpoons 2HBr+S$. If sulphur dioxide be used in place of hydrogen sulphide a pale yellow homogeneous liquid is obtained: $SO_2+Br_2+2H_2O\rightleftharpoons 2HBr+H_2SO_4$. When this liquid is distilled an aq. soln. of hydrogen bromide is obtained. The reaction is reversible, sulphuric acid decomposes hydrogen bromide into bromine and sulphur dioxide. According to C. Harms, hydrobromic acid is formed by the action of bromine water and sulphur.

Hydrogen bromide cannot be satisfactorily prepared by the action of sulphuric acid upon potassium bromide as in the preparation of hydrogen chloride by the action of sulphuric acid upon potassium chloride unless very special precautions are taken.[8] When the attempt is made, under ordinary conditions, colourless hydrogen bromide is first given off, but the issuing gas immediately acquires a yellow colour, and then a brown tinge, showing that bromine is also evolved. The issuing gas also contains sulphur dioxide. Hence not only does the reaction: $KBr+H_2SO_4=KHSO_4+HBr$ take place, but also the consecutive reaction: $2HBr+H_2SO_4=SO_2+Br_2+2H_2O$, and the method is accordingly impracticable. If dil. sulphuric acid be employed with the idea of preventing an appreciable decomposition of the hydrogen bromide, the yield of hydrogen bromide is very small. If phosphoric acid be used in place of sulphuric acid, because phosphoric acid does not deoxidize so readily as sulphuric acid, the reaction: $KBr+H_3PO_4=KH_2PO_4+HBr$, is rather slow. Other salts have been used in place of potassium bromide—*e.g.* barium or calcium bromide; and zinc bromide. W. Feit and K. Kubierschky warm a soln. of potassium bromide in sulphuric acid of sp. gr. 1·41; and distil it until sulphuric acid begins to pass over. The liquid product is then re-distilled and the fraction which passes over about 126° collected. It has a sp. gr. about 1·49; contains about 48 per cent. of HBr; and is said to be free from bromine and sulphur dioxide.

Hydrogen bromide is also formed when some of the metallic bromides are reduced to metals in a current of hydrogen. Thus, at a red heat with silver bromide: $2AgBr+H_2=2HBr+2Ag$; and similarly, hydrobromic acid is formed when silver bromide suspended in water is treated with hydrogen sulphide.[9] Hydrogen bromide is sometimes made by the action of bromine on hydrocarbons[10]—*e.g.* naphthlene, $C_{10}H_8$; benzene, C_6H_6; anthracene, $C_{10}H_{10}$; paraffin; etc., the gas is then more or less contaminated with organic products. H. Erdmann's process is as follows:

Pour 100 grms. of dry benzene into a flask containing a few grms. of anhydrous ferrous bromide, or fine iron powder, or aluminium powder. Run 135 c.c. of bromine very gradually into the flask by means of a separating funnel with the tube drawn out to a fine point. The flask should be put in cold water to prevent bromine or benzene from distilling over. When about half the bromine has been added, the reaction runs so quietly that the cooling is no longer necessary. The reaction is symbolized: $C_6H_6+2Br_2=C_6H_4Br_2+2HBr$. To scrub the gas from benzene and bromine vapours, pass the gas through a large U-tube, one leg of which is filled with ferric bromide, $FeBr_3$, and the other with anthracene. For hydrobromic acid pass the gas into water cooled with a freezing mixture.

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§ 8. The Preparation of Hydrogen Iodide and Hydriodic Acid

B. Courtois (1813)[1] first prepared hydrogen iodide, HI, without recognizing its nature. Hydrogen does not unite with iodine at ordinary temp.; but in his historic memoir on iodine, J. L. Gay Lussac (1814) showed that if hydrogen and iodine vapour be passed through a red-hot tube, union does occur. H. Davy also prepared *le gaz de l'iode*, and E. Turner showed in 1824 that the reaction occurs at ordinary temp. in the presence of platinum black or platinum sponge. According to B. Corenwinder, the two gases unite at 300° or 400°. The combination, said P. Hautefeuille (1867), is only partial because the same catalytic agent decomposes hydrogen iodide. The reaction is therefore reversible as previously discussed. M. Bodenstein claimed a 90 *per cent.* yield, and E. Beckmann and P. Wäntig a 60 *per cent.* yield. According to G. Lemoine,[2] union does not occur in the cold under the influence of light. A little hydrogen iodide is formed when iodine water is exposed to sunlight, or when heated: $2H_2O+2I_2 \rightleftharpoons 4HI+O_2$. According to C. F. Schönbein, dil. hydrogen peroxide forms a little hydrogen iodide and oxygen: $H_2O_2+I_2=2HI+O_2$.

Hydrogen iodide can also be made by the action of iodine on many hydrocarbons, and other hydrogen compounds—phosphine, aq. hydrogen sulphide and ammonia.[3] The preparation of an aq. soln. of hydrogen iodide by the hydrogen sulphide process is as follows:

Add about 3 grms. of powdered iodine to 250 c.c. of water in a 500 c.c. flask and pass a stream of hydrogen sulphide slowly into the mixture. In a few minutes all the iodine will have dissolved owing to the reaction: $H_2S+I_2=S+2HI$. Add more powdered iodine, and continue the passage of the gas. Repeat the operations until about 20 grms. of iodine have been added. Transfer 30 grms more iodine—50 grms. in all—to the flask. In about half an hour the iodine will all have dissolved in the hydrogen iodide already formed. Continue passing hydrogen sulphide until the brown colour of the soln. disappears, showing that all the iodine has been transformed into hydrogen iodide. Pass a rapid stream of carbon dioxide or hydrogen through the warm soln. to drive off the hydrogen sulphide. Shake the soln. to coagulate the sulphur; and remove the sulphur from the soln. of filtration through glass wool. The soln. can be further purified by distillation; collect the fraction which boils between 125° and 130°. This soln. contains about 50 per cent. of hydrogen iodide. A more conc. soln. can be made by passing gaseous hydrogen iodide into cold water, or, better, into a soln. of hydrogen iodide made as just described.

J. R. Joss modified the process by shaking granulated lead with water and iodine until the liquid is colourless; hydrogen sulphide is then passed through the liquid, and the clear liquid decanted. E. Bodroux mixed the calculated quantity of iodine

with a paste made of barium peroxide and water: oxygen is evolved, and barium iodide is formed. More iodine is added to the filtered liquid containing barium iodide. When sulphur dioxide is passed through the liquid, barium sulphate is precipitated: $BaI_2+I_2+SO_2+2H_2O=BaSO_4+4HI$. The colourless liquid is distilled. If a soln. of iodine in copaiba balsam is heated, or if colophonium or resin be heated with iodine, hydrogen iodide is formed. J. H. Kastle and J. H. Bullock[4] heated a mixture of iodine, resin, and sand, and A. Étard and H. Moissan, a mixture of iodine with an equal bulk of resin. Hydrogen iodide is copiously evolved and a brownish liquid also distils over, and this is collected in a small receiver.

Hydrogen iodide is prepared by the action of reducing agents on iodine and water. The iodine takes hydrogen, and the reducing agent the oxygen of the water. J. L. Gay Lussac used phosphorus.[5] J. P. J. d'Arcet, phosphorous acid; C. Méne, calcium hypophosphite; E. Soubeiran, dil. sulphurous acid, sulphites, arsenious acid, and stannous salts: $Na_2SO_3+H_2O+I_2=2HI+Na_2SO_4$; and J. H. Gladstone used sodium thiosulphate. In the latter case, sodium iodide and tetrathionate, $Na_2S_4O_6$, are formed, and the oxidation is so slow that the use of thiosulphate is not recommended. When phosphorus[6] is employed, it is generally assumed that phosphorus iodide is first formed, and that this is decomposed by the action of water. B. Corenwinder found that some phosphine, PH_3, is produced when hydrogen iodide is prepared by the action of water on phosphorus tetra iodide, P_2I_4, and to prevent this, the operation is conducted by mixing one part of red phosphorus with 20 parts of iodine in a warm dry flask, and gradually adding four parts of water from a dropping funnel to the products of the reaction. This is a modification of the process employed for the preparation of hydrogen bromide which is rendered necessary, because bromine is liquid and iodine solid. Phosphorus tri-iodide, PI_3; tetra-iodide, P_2I_4; or penta-iodide, PI_5, is formed. Each of these reacts with water, forming hydrogen iodide: $PI_5+4H_2O=H_3PO_4+5HI$; etc. An excess of iodide is recommended by L. Meyer in order to avoid the formation of phosphorous acid: $2P+3I_2+6H_2O=2H_3PO_3+6HI$, and the formation of phosphine. With an excess of iodine the main reaction is symbolized: $2P+5I_2+8H_2O=2H_3PO_4+10HI$. Lothar Meyer mixed 100 grms. of iodine with a tenth of its weight of water in the flask, and by means of a dropping funnel gradually added a "slip" made by mixing 5 grms. of red phosphorus with twice its weight of water. The idea is here to keep the iodine always in excess so as to avoid the formation of phosphine, which is liable to occur when the phosphorus is in excess. M. Adams says time can be saved by cooling the flask by a freezing mixture while the phosphorus is being added; in this way the operation requires but a few minutes when half an hour is needed without the cooling. A. Bannow dropped a soln. of iodine in conc. hydriodic acid on solid phosphorus; and N. A. E. Millon used a mixture of phosphorus, potassium iodide, iodine, and water—cooled if necessary to reduce the violence of the reaction: $2P+5I_2+4KI+8H_2O=14HI+2K_2HPO_4$. Free iodine is removed from the gas by passing the hydrogen iodide through a small U-tube containing a little water, and then through a tower packed with red phosphorus and glass wool. A little phosphonium iodide may be formed in the tower. The gas can be dried by passing it through a tube containing calcium iodide; or, according to V. Meyer, phosphorus pentoxide. Calcium chloride is partially decomposed by the gas. According to A. van den Berghe, hydrogen iodide is formed when a conc. soln. of the acid is slowly dropped on solid phosphorus pentoxide, and the gas washed with a conc. soln. of calcium iodide.[7] Hydrogen iodide cannot be collected over mercury because the mercury is attacked; it can be collected by the upward displacement of air.

As with hydrogen bromide, but unlike hydrogen chloride, hydrogen iodide cannot be satisfactorily made by the action of sulphuric acid upon potassium iodide. According to the conditions of the experiment, sulphuric acid can be reduced by hydrogen iodide to sulphur dioxide, free sulphur, or even to hydrogen sulphide. In the latter case the reaction is symbolized: $H_2SO_4+8HI\rightleftharpoons 4H_2O$

$+4I_2+H_2S$. A dil. soln. of hydriodic acid is formed by passing hydrogen sulphide into iodine water: $H_2S+I_2+Aq.=2HI+S+Aq$. R. M. Glover used barium iodide and sulphuric acid. According to B. Lepsius,[8] molten phosphoric acid, in place of sulphuric acid, gives very fair results with potassium iodide. W. Stevenson used barium iodide. Gaseous hydrogen iodide is usually made by the decomposition of phosphorus iodide.

The purification of gases by fractional solidification.—It is comparatively easy to purify solids by crystallization and liquids by distillation; but with gases, the air which clings obstinately to the walls of the vessel requires the loss of a comparatively large proportion of gas if it is to be washed out of the apparatus, and this the more, if the gas is scrubbed in calcium chloride tubes; or in tubes containing phosphorus pentoxide and glass wool, or sulphuric acid and pumice-stone; or in tubes containing special absorbents for removing impurities. With the more costly gases, this necessary washing of the apparatus free from air is a serious inconvenience. In the more recent processes for purifying some gases,[9] the impure gas is cooled to a progressively decreasing temp., whereby moisture and gaseous impurities are frozen out, and finally the gas under investigation is liquefied or frozen solid. The apparatus is then exhausted by the mercury pump. This removes gaseous impurities and air which may have been dissolved by the liquefied or solidified gas. The temp. is then allowed to rise, the solid liquefies, then vaporizes, and is finally collected where desired. The constancy of the b.p. is a criterion of the purity of the gases. The method recommended for hydrogen iodide is as follows:

The apparatus generating the hydrogen iodide is connected with the cylindrical glass vessel *A*, Fig. 12, then with the two U-tubes, *B* and *C*. These tubes have bulbs alternating with capillary portions. All these tubes are inclosed in double-walled Dewar flasks containing a mixture of acetone and solid carbon dioxide which produces a temp. of $-32°$. Nearly all the moisture is precipitated as ice in the first tube *A*, and the remaining traces are deposited on the extensive surface of the first U-tube, where the gas is well churned by the alternate contraction and enlargement of the stream. The tube *C* serves as a check on the other two. It communicates by a 3-way cock *D* with a condenser *E*, and the tube *F*. The condenser *E* is cooled to $-80°$ and connected with the mercury pump. The pump is worked so as to pull the mixture of air and hydrogen iodide coming from the gas generator through the apparatus. The water vapour is condensed in the tubes *A*, *B*, and *C*; the hydrogen iodide solidifies in the condenser *E*; and the air is drawn off by the pump. When enough hydrogen iodide has solidified, the 3-way cock is turned so as to put the condenser in communication with the efflux tube, *F*, and the system is exhausted. The cooling agent is removed from the condenser, when the hydrogen iodide melts, evaporates, and passes down the efflux tube to where it is required.

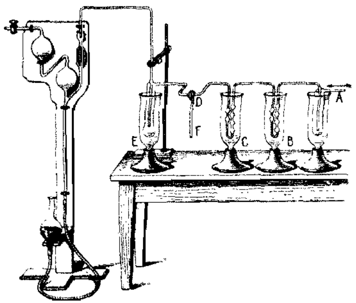

FIG. 12.—The Purification of Hydrogen Iodide by Fractional Solidification.

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§ 9. The Physical Properties of the Hydrogen Chloride, Bromide, and Iodide

The hydrogen halides are all colourless gases which fume strongly in moist air; they have an irritating odour, and an acid taste. According to M. von Pettenkofer and K. B. Lehmann,[1] animals exposed to air containing 3·4 per cent. of hydrogen chloride for $1\frac{1}{2}$ hrs. were seriously affected; rats withstood the gas best; cats and rabbits died next day from this dose. A strong man can stand for a short time air containing only 0·05 per cent. of the gas, and the limit for workmen who have become accustomed to it is put at 0·1 per cent. The hydrogen halides can all be condensed to colourless liquids, and frozen to white crystalline solids.

Vapour density and specific gravity.—J. Dalton in 1808 gave the density of hydrogen chloride as 1·23; most subsequent observers found rather higher numbers. A. Leduc (1897), P. A. Guye and G. Ter-Gazarian (1907), O. Scheuer (1910), R. W. Gray and F. P. Burt (1911)[2] obtained the values 1·2692, 1·2684, 1·2681, and 1·2679 respectively for the density of hydrogen chloride when that of air is unity – temp. and press. normal, latitude 45°, and sea level. The corresponding weights in grams of a normal litre are 1·6408, 1·6308, 1·6398, 1·6394, and 1·63915 grms. respectively. There is no sign of a polymerization at low temp.; H. Biltz found a density of 1·197 at −77·1°—the normal value is 1·268. F. F. Rupert measured the density of the vapour of hydrogen chloride in the presence of its own liquid, expressed in grms. per c.c. at

	51°	40°	20°	0°	−15°	−30°	−50°
Gas, HCl	0·278	0·181	0·0974	0·0539	0·0343	0·0238	0·0125

H. St. C. Deville found indications of free chlorine in the gas which had been cooled abruptly from 1500°; but V. Meyer and his co-workers obtained a normal density at temp. up to 1500°, and at 2500°, according to M. Bodenstein and A. Geiger, the percentage dissociation amounts to only 1·3 per cent.; and at 1000°, 0·00134 per cent., as indicated in Table III. E. Moles obtained 3·6442 ± 0·00013 for the weight of a normal litre of hydrogen bromide; W. J. Murray 3·6440 ± 0·005 grms.; and C. K. Reiman, 3·6442 ± 0·0002 grms.

C. Löwig (1829)[3] found the vapour density of hydrogen bromide to be 2·71; H. Biltz found a normal density 2·77 in the vicinity of its b.p., at −15°, 2·989;

and at $-28°$, 2·873, when the theoretical density referred to air unity, is 2·7926; the weight of a litre of this gas at 0° and 760 mm. is 3·6167. Hydrogen bromide dissociates at elevated temp.—at 1000° the dissociation is 0·144 per cent., and at 2000°, 3·4 per cent as indicated in Table III. According to J. L. Gay Lussac,[4] the density of hydrogen iodide is 4·4429 at 0°. The theoretical value (referred to air unity) is 4·415. H. Biltz found 4·569 at $-17°$, and 4·619 at $-24·9$, and K. Strecker, 4·443 at 120°. These values may be regarded as indicating that the vapour density of hydrogen iodide over this range of temp. is normal. Indeed, excluding hydrogen fluoride, the vapour densities of the hydrogen halides are normal at their b.p. At 290°, hydrogen iodide is dissociated about 6·2 per cent., and at 1000°, 29 per cent. as indicated in Table III.

The sp. gr. of liquid hydrogen chloride between its m.p. and b.p., according to D. McIntosh and B. D. Steele,[5] is

Temp. .	−104·5	−101·2	−98·2	−92·2	−89·8°	−85·8°	−83·1
Sp. gr. . .	1·2438	1·2347	1·2242	1·2127	1·2038	1·1937	1·1812

G. Ansdell (1880) and F. F. Rupert (1909) have measured the sp. gr. of liquid hydrogen chloride at higher temp.; the latter obtained

	51	40	20	0	15	30	−50°
Sp. gr. . .	0·572	0·707	0·839	0·929	0·984	1·032	1·090

The rapid increase in the sp. gr. with a falling temp. corresponds with a large expansion with a rising temp. The mol. vol. of hydrogen chloride at its b.p. is 30·8, and the corresponding values for hydrogen and chlorine are 5·5 and 25·3—H. Kopp's value for chlorine, calculated from the mol. vol. of organic compounds, is 22·8.

The sp. gr. of liquid hydrogen bromide, according to D. McIntosh and B. D. Steele,[6] is

	−91	87	−81	77	73	−69°
Sp. gr. . .	2·245	2·229	2·206	2·191	2·176	2·160

and they represent the whole range of sp. gr. D at $T°$ absolute by the formula $D=2·157+0·0088437(204·3-T)$. At 10°, L. Bleekrode gives the value 1·63. The mol. vol. at the b.p. is 37·4; Kopp's rule gives 33·4. D. McIntosh and B. D. Steele also give the following values for the sp. gr. of liquid hydrogen iodide:

	−51°	−47	−43°	−39°	−35	31°
Sp. gr. . .	**2·863**	**2·847**	**2·830**	**2·813**	**2·796**	**2·779**

and the interpolation formulæ for the sp. gr. D at $T°$ absolute, $D=2·799+0·0120357(237·4-T)$. The mol. vol. at the b.p. is 45·7; the value 43·3 is obtained by Kopp's rule.

Deviations from the ideal gas law.—The deviation in the density of gaseous hydrogen chloride 1·6392 under normal conditions from the theoretical value 1·6284 (referred to air unity) is because hydrogen chloride is more strongly compressed under atm. press. than corresponds with an ideal gas. R. W. Gray and F. P. Burt[7] have measured the pv-values for hydrogen chloride at 0°, and found

p .	829·50	720·78	515·35	384·13	289·39	223·95	157·57 mm.
v .	66·012	76·072	106·642	143·259	190·331	246·117	349·978 c.c.
pv .	*54757*	*54831*	*54958*	*55030*	*55080*	*55118*	*55146*

They found the variation of pv per unit of press. decreases as the press. falls, and the rate of decrease if greater at lower press. If v_0 and v_1 denote the volumes occupied by the same mass of gas at press. p_0 and p_1, R. W. Gray and F. P. Burt give 55213 for p_0v_0 and 54803 for p_1v_1, and the deviation of the gas from Boyle's law per atm. between the press. limits 0 and 1 atm. is defined by the expression $A_0'(p_0v_0-p_1v_1)/p_0v_0(p_1-p_0)$. E. Moles found for hydrogen bromide $(pv)_0/(pv)_1=1+\lambda$, where $\lambda=0·00931$; and C. K. Reiman, $\lambda=0·00927$—the value for oxygen is 0·00097.

P. A. Guye represents the relation between compressibility (pv) and press., p, by the formula $(pv)=1+a+ap+bp^2$, where a, a, and b are constants.

The surface tension and viscosity.—The surface tension σ, and the molecular surface energy, $(Mv)^{\frac{2}{3}}$, of R. Eötvos was determined for liquid hydrogen chloride by D. McIntosh and B. D. Steele[8]:

Temp.	−109·9°	−101·3°	−92·9°	−89·8	−84·8°	−80·4°
σ	27·874	26·251	24·718	24·046	23·467	22·409
$\sigma(Mv)^{\frac{2}{3}}$	263·68	250·80	239·00	233·65	229·30	221·03

and the temp. coeff. $d\sigma(Mv)^{\frac{2}{3}}/dT=1·47$, whereas with normal fluids, the value is 2·12; hence, it is inferred that the liquid is associated. The viscosity of liquid hydrogen chloride η referred to water at 22° unity is 0·590 at 160·8° K.; 0·530 at 171·7° K., and 0·477 at 188·2° K. The viscosity of liquid hydrogen bromide at its b.p. is 0·83, and the temp. coeff., 0·58 per cent.; for liquid hydrogen iodide, the viscosity at the b.p. is 1·35 with a temp. coeff. of 0·70 per cent. According to P. Walden, the surface tension of liquid hydrogen bromide in dynes per cm. is 30·191 at 181·8° K.; and D. McIntosh and B. D. Steele's formula for the surface tension at $T°$ K. is $\sigma=30·19(1-0·00314T)/(1-0·00314\times181·8)$. The surface tension of liquid hydrogen iodide is 29·06 dynes per cm. at −47·7°, and the surface tension σ at $T°$ K. is $\sigma=20·96(1-0·00265T)/(1-0·00265\times225·3)$. The specific cohesion, a^2, of liquid hydrogen bromide at 186° K. is 2·67, and at $T°$ K. the value of a^2 = 2·67(1−0·00274T)/(1−0·00274×186); and of liquid iodide at −47·7° is 2·01, and it varies so that $a^2=2·08(1-0·00230\times225·3)$. The temp. coeff. of the molecular surface energy of liquid hydrogen bromide $d\sigma(Mv)^{\frac{2}{3}}/dT$ between −91° and −63° is nearly 2·03. The value for liquid hydrogen iodide is 1·99. These numbers are very close to those required for normal liquids. Hence, this indicates that the liquids are not associated. The application of several other of Walden's rules also makes it highly probable that liquid hydrogen bromide has the simple formula HBr, and liquid hydrogen iodide, HI. The intrinsic press. K of the four liquid hydrogen halides, calculated from J. Stefan's rule $(K-p)v_b=\frac{1}{2}M\lambda$, where p is negligibly small in comparison with K; v_b, is the mol. vol. at the b.p.; M, is the mol. wt.; and λ, the latent heat of evaporation:

	HF	HCl	HBr	HI
Intrinsic press. (about)	7300	2615	2240	2230 atm.

The intrinsic press. thus decrease with increasing at. wt.; the opposite applies to the liquid halogens themselves.

The coeff. of viscosity of hydrogen chloride gas is 0·000141; the free path, 0·0000071 cm.; the collision frequency 5670×10^2 per second; molecular diameter, $1·70\times10^{-7}$ cm.; the coeff. of condensation from gas to liquid, or D_{gas}/D_{liquid} =0·00282. The square root of the mean square of the molecular velocity of hydrogen chloride is $4·34\times10^4$ cm. per sec., and the arithmetical mean, 4×10^4 cm. per sec.

The critical constants.—In 1823, H. Davy and M. Faraday[9] liquefied hydrogen chloride by sealing ammonium chloride in one leg of a **W**-shaped tube, and sulphuric acid in the bend. By suitably turning the tube over, everything was collected in one leg; the empty end was placed in a freezing mixture. Colourless liquid hydrogen chloride was obtained. M. Faraday did not succeed in solidifying hydrogen chloride, but he did both liquefy and solidify hydrogen bromide and hydrogen iodide by cooling the gases at atm. press. with a mixture of solid carbon dioxide and ether. K. Olschewsky solidified hydrogen chloride in 1884. Numbers for the critical temp. of hydrogen chloride[10] vary from 51·25° to 52·3°; the critical press. between 83·0 and 96·0 atm., and the critical density between 0·40 and 0·61. T. Estreicher gives the critical temp. of hydrogen bromide between 90·4° and 91·3°; E. Moles found 89·80°, which may be taken as the best representative value. T. Estreicher estimated that the critical temp. of hydrogen iodide lies between 150·7° and 150·4°. These numbers agree with P. Walden's relations: $\beta T_c=1·16$; and $kT_c=0·94$,

where T_c denotes the critical temp. in absolute units; β is the temp. coeff. of the surface tension; and k the temp. coeff. of the specific cohesion. For example, for hydrogen iodide, =0·00265; and k=0·00230. The critical press. are not known, but P. Walden's rule $p_c=6{\cdot}5\sigma/\log T_b-0{\cdot}012T_b$, where σ denotes the surface tension at the b.p., furnishes for hydrogen bromide, 69 atm., and for hydrogen iodide, 71·0 atm. The critical density, D_c, of hydrogen bromide is 0·807 and of hydrogen iodide 1·046; these numbers are calculated from P. Walden's rule, $D_c=0{\cdot}3738D_b$, where D_b denotes the sp. gr. at the b.p.—2·157 for liquid hydrogen bromide, and 2·799 for liquid hydrogen iodide. E. Moles has compared the critical temp. calculated by a number of other formulæ, with the observed values, and found the result is in agreement with C. M. Guldberg's and P. A. Guye's rules, but not with W. R. Fielding's.

The boiling and melting points.—The b.p. of liquid hydrogen chloride[11] at atm. press. is given as −82·9° by D. McIntosh and B. D. Steele, and as −83·7° by T. Estreicher. The m.p. of hydrogen chloride is −111·1° according to T. Estreicher, and −112° according to E. Beckmann and P. Wäntig. The b.p. of hydrogen bromide is given at −64·19° (738·2 mm.) by T. Estreicher, and −68·7° (760 mm.) by D. McIntosh and B. D. Steele; the m.p. of hydrogen bromide is −86° according to A. Ladenburg and C. Krügel, and −87·9° according to T. Estreicher; the latter gives −88·5° for the f.p. The b.p. of liquid hydrogen iodide is given as −34·14° (730·4 mm.) and −34·12° (739·8 mm.) by T. Estreicher, and −36·7° by A. Ladenburg and C. Krügel. The m.p. of solid hydrogen iodide is −50·8° according to T. Estreicher and D. McIntosh and B. D. Steele; and −51·5° according to A. Ladenburg and C. Krügel.

H. M. Vernon (1891)[12] has pointed out that the b.p. of liquids sometimes give a clue as to their mol. wt. For example, hydrogen iodide boils at −25°, hydrogen bromide at −73°, hydrogen chloride at −100°, and it might be expected that hydrogen fluoride would boil about −120°; as a matter of fact, it boils about 19·4°, showing that the molecules of the liquid are probably more complex than is the case with the other three haloid acids. H. Biltz observed no signs of polymerization with the other haloid acids: at −77° with hydrogen chloride; at −28° with hydrogen bromide; or at −25° with hydrogen iodide. The hydrides of oxygen, sulphur, selenium, and tellurium furnish another illustration of H. M. Vernon's rule.

The vapour pressure.—D. McIntosh and B. D. Steele[13] give for the vap. press. of liquid hydrogen chloride between the b. and m. p.:

	−109·9°	−101·3°	−92·9°	−85·9°	−83·2°	−80·5°
Vap. press.	141	245	430	648	748	868 mm.

M. Faraday continued the measurements up to 4°, and to 50·56°.

	−73·33°	−45·56°	−17·78°	0°	18·1°	33·4°	50·56°
Vap. press.	1·80	6·30	15·04	26·20	41·8	58·85	85·33 atm.

D. McIntosh and B. D. Steele measured the vap. press. of solid and liquid hydrogen bromide of m.p. −86°:

	−104·2°	−100·7°	−96·3°	−87·1°	−83°	−76·7°	−70·7°	−68·4°
Vap. press.	96	142	185	284	357	501	682	775 mm.

The vap. press. of solid and liquid hydrogen iodide of m.p. −35·7° were also found to be:

	−77·9°	−74°	−54·6°	−50°	−45·8°	−30·5°	−35·9°
Vap. press.	74	90	303	376	539	743	769 mm.

M. Faraday gave 2·9 atm. at −32°; 3·97 atm. at 0°; and 5·86 at 15·5°.

The heats of fusion and vaporization.—From the lowering of the f.p. of cymene and toluene by the soln. of liquid hydrogen chloride, E. Beckmann and P. Wäntig[14] calculate the heat of fusion of hydrogen chloride as 10·3 cals. per gram; of hydrogen bromide, 7·44 cals.; and of hydrogen iodide, 4·13 cals. D. McIntosh and B. D. Steele calculate from Clapeyron and Clausius' equation $d \log p/dT=\lambda/RT^2$, for the mol. ht.

of vaporization of hydrogen chloride at its b.p., 3·54 Cals; of hydrogen bromide, 4·15 Cals.; and of hydrogen iodide, 4·94 Cals. P. H. Elliott and D. McIntosh found experimentally 3·56 Cals. for hydrogen chloride; 4·15 Cals. for hydrogen bromide; and 4·48 Cals. for hydrogen iodide. T. Estreicher and A. Schnerr find 3·6 Cals. for the chloride; 3·939 Cals. for the bromide; and 4·3318 Cals. for the iodide. The corresponding heats of vaporization per gram are 98·7 cals. for the chloride; 48·68 cals. for the bromide; and 33·9 cals. for the iodide. Trouton's rule for hydrogen chloride gives the value 19·0. This value, slightly lower than the normal, may mean a slight association. K. Tsuruta prefers the relation: $\lambda=T(v_g-v_1)dp/dT$, where v_g and v_1 respectively denote the sp. vol. of gas and liquid for calculating the heat of vaporization at higher temp. and press., because the volumes of gaseous and liquid hydrogen chloride can then no longer be neglected. He thus obtains for the heat of vaporization at 4°, from the data by G. Ansdell, 61·02 cals., and at 49·9°, 23·49 cals. A. Reis gives for the heat of sublimation of hydrogen chloride 3·6 Cals.; for hydrogen bromide, 4·7 Cals.; and for hydrogen iodide, 5·0 Cals.

Specific heats.—According to H. V. Regnault,[15] the mean sp. ht. of hydrogen chloride gas at constant press. is $C_p=0·1867$ between 22° and 214°; and for the ratio of the two sp. ht. $C_p/C_v=1·400$ at 100°. According to W. Nernst and M. Pier, the mol. ht. of hydrogen chloride is the same as that of any gas with diatomic molecules difficult to dissociate—*e.g.* oxygen, nitrogen, carbon monoxide, etc.—and up to the highest temp. 1900° the mean sp. ht. *between* 0° and θ° is $C_p=6·885+0·000045\theta$; and $C_v=4·90+0·000045\theta$; and at θ°, $C_p=6·885+0·00009\theta$; and $C_v=4·90+0·00009\theta$. K. Strecker found the ratio of the two sp. ht. of hydrogen bromide to be 1·431, a value nearly the same as that of hydrogen; and from the relation $C_p-C_v=R$ he calculates for $C_p=0·0820$; and $C_v=0·0573$ between 20° and 100°; according to P. A. Müller at press. between 752·4 and 293·9 mm. and temp. between 37·8° and 10·1°, the ratio of the two sp. ht. is 1·3647. For the mol. ht. of hydrogen bromide *between* 0° and θ°, F. Haber gives $C_p=6·89+0·000045\theta$; and M. Bodenstein and A. Geiger, for the true mol. ht. at T°, find $C_p=6·5+0·0017T$; and $C_v=4·5+0·0017T$. For the ratio of the two sp. ht. of hydrogen iodide between 20° and 120°, K. Strecker finds $Cp/C_v=1·397+0·001$, and hence calculates $C_p=0·0550$; and $C_v=0·0394$. From K. Strecker's values it follows that the mol. ht. of hydrogen iodide at T° are $C_p=6·5+(0·0016+0·0003)T$, and $C_v=4·5+(0·0016+0·0003)T$. According to W. Nernst, the mol. ht. of hydrogen iodide is nearly the same as that of hydrogen chloride.

Heats of formation.—J. Thomsen [16] gives for the heat of formation of gaseous hydrogen chloride from its gaseous elements H+Cl=HCl+22·001 Cals.; P. A. Favre and J. T. Silbermann give 23·783 Cals.; and J. J. B. Abria gives 24·010 Cals. M. Berthelot gave 22·0 Cals. at ordinary temp. and 26·0 Cals. at 2000°. J. Thomsen gives 8·44 Cals., and P. A. Favre 7·108 Cals., for the heat of formation of gaseous hydrogen bromide from liquid bromine and hydrogen; and for $H+Br_{gas}=HBr$ at 60°, 12·3 Cals., when hydrogen chloride under the same conditions is 22·04 Cals. J. Thomsen considers the difference 9·74 Cals. to represent the higher affinity of chlorine for hydrogen. M. Berthelot gives $H+Br_{gas}=12·3$ Cals.; $H+Br_{liquid}=8·6$ Cals.; and $H+Br_{solid}=7·3$ Cals. M. de K. Thompson gives 8·4 Cals. for the heat of formation, or total energy of formation and 11·950 Cals. for the free energy of formation of hydrogen bromide from measurements of the potential of the cell $H_2|HBr|Br_2$. For hydrogen chloride the corresponding numbers are respectively 22·3 and 22·2 Cals. For further observations on free energy see "the e.m.f. of cells." M. Berthelot gives for the heat of formation of hydrogen iodide $H+I_{solid}=HI_{gas}$, −0·64 Cal., and $H+I_{gas}=HI_{gas}+0·4$ Cals. For solid iodine and hydrogen, J. Thomsen gives 6·036 Cals., and for gaseous hydrogen iodide, at the b.p. of iodine, 180°, −0·436 Cal. M. Bodenstein calculates for $H+I_{gas}=HI_{gas}$ at ordinary temp. +0·4 Cal. from M. Berthelot's data, and 0·7 Cal. from J. Thomsen's data. F. Haber calculates 0·096 Cal. from the relation between the equilibrium constant

and temp.—*vide* §4. For the heats of formation in soln., etc., see the respective acids; and for the heats of formation from molecules and atoms of the elements, see "Thermo-chemistry." S. J. Bates and H. D. Kirschman found the **free energy** of formation of hydrogen chloride is −22700 cals., hydrogen bromide, −12592 cals., and hydrogen iodide, +310 cals.

Optical constants.—P. L. Dulong[17] found the refractive index of hydrogen chloride for white light to be 1·000447; and E. Mascart, the refractive indices of the hydrogen haloids for the *D*-line: 1·000444 for HCl; 1·000570 for HBr; and 1·000906 for HI. L. Bleekrode found the index of refraction of liquid hydrogen chloride to be 1·256 for the *D*-line, and 1·00045 for the gas. Accordingly, the specific refraction of the liquid by J. H. Gladstone and T. P. Dale's formula is 0·300; and of the gas, 0·277. H. A. Lorentz and L. Lorenz's formula furnishes 0·19 for the liquid, and 0·185 for the gas. C. and M. Cuthbertson obtained for the refractivities, $(\mu-1)\times10^6$, at 0° and 760 mm., for the green mercury line $\lambda=546·1\mu\mu$, are 351·1 for HCl; 614·9 for HBr; and 925·8 for HI. The results for what they call the dispersion $(\mu-1)\times10^6D/76D_0$, where D denotes the density of the gas at $\theta°$, and D_0 its density at 0°, are indicated in Table V. W. Sellmeyer's formula for

TABLE V.—DISPERSION OF THE HYDROGEN HALIDES.

Wave-length, $\mu\mu$	HCl	HBr	HI
479·99	451·87	621·60	939·00
520·91	449·30	617·04	930·15
576·95	446·66	612·56	921·06
643·85	444·44	608·78	913·34
670·78	443·75	607·52	910·87

the relation between the refractive index μ and the frequency n of the light vibration when n=the velocity V ÷ the wave-length λ, is $\mu-1=C/(n_0^2-n^2)$, where the values of the constant $C\times10^{-27}$ are respectively 4·6425, 5·1446, and 5·7900 for hydrogen chloride, bromide, and iodide; and of the constant $n_0^2\times10^{-27}$, 10664·0, 8668·4, and 6556·4 respectively for the same three gases.

Spectrum.—According to J. Tyndall,[18] hydrogen chloride and hydrogen bromide absorb heat rays. W. H. Julius found that hydrogen chloride had an absorption band for the wave-length 3·68μ; and K. Angström and W. Palmaer at 3·41μ. W. de W. Abney and E. R. Festing found liquid hydrochloric acid had very feeble absorption lines in the ultra-red at 732, 741, 845, 867, and 949$\mu\mu$.

P. Drude[19] showed that the optical dispersion of crystals is best explained by assuming that the infra-red absorption and emission bands are due to the vibrations of electrically charged atoms and molecules, rather than to the oscillations of electrons inside the atoms. P. Drude's views were confirmed when it was shown by E. Madelung, A. Einstein, W. Dehlinger, etc., that the frequencies of the Reststrahlen can be roughly computed from the elastic constants of the crystals. N. Bjerrum also showed that the structure of the infra-red absorption bands of gases confirms M. Planck's quantum theory. In 1892, Lord Rayleigh proved that if an oscillator emits and absorbs light of frequency ν_0, and rotates with a frequency ν_r about an axis perpendicular to the direction of vibration, the emitted and absorbed light should be divided between the frequencies $\nu_0\pm\nu_r$ with a corresponding broadening of the spectrum lines. In confirmation, N. Bjerrum showed that in the infra-red absorption spectra of gases there is a broadening of the magnitude to be expected from the molecular rotations. Unlike the bands in the infra-red, (i) the lines in the visible and ultra-violet spectra are due to the vibrations of electrons inside the atoms; and (ii) the atoms do not rotate with angular velocities comparable with those of the molecules.

P. Drude's hypothesis explains how in a diatomic gas like hydrogen chloride,

[C] there should be only one absorption band due to the vibrations of the two toms along their line of centres. If a rotation occurs only about the axes perendicular to the line of centres, then the distribution of the angular velocities ads to the assumption that there should be a doublet with a maximum correonding with the most probable angular velocity of the molecules at the temp. in uestion. The infra-red spectrum of hydrogen chloride has a doublet with maxima t $3\cdot40\mu$ and $3\cdot55\mu$ at room temp. From the separation of the maxima, N. Bjerrum lculates that the moment of inertia of the HCl-molecule is $5\cdot4\times10^{-40}$ grms. per q. cm.; E. C. Kemble, that the distance between the atomic centres is $1\cdot84\times10^{-8}$ cm.; and D. A. Goldhammer, that the molecular diameter is $3\cdot0\times10^{-8}$ cm. bservations of W. Burmeister and E. von Bahr confirm the frequent appearance f double bands in the infra-red spectra of gases, and the separation of the maxima ith temp. in accord with N. Bjerrum's theory.

N. Bjerrum predicted that more complex gases should furnish triplets, but this not in accord with observations with water vapour and carbon dioxide. I. A. Lorentz, and W. Nernst, however, have suggested that the molecule cannot state except with such angular velocities as make the energy an integral multiple f $h\nu$; and hence N. Bjerrum concluded that the absorption in the extreme infra-red, y, beyond 40μ, supposed to be due to the direct action of molecular rotations, ust be broken up into a series of equally spaced narrow bands, while in the near nfra-red, the vibrations mainly due to the atoms will be similarly made up of a ries of equally spaced fine lines which are really bands if observed with an apparatus f high resolving power. The predictions have been verified by N. Bjerrum and . Eucken. The subject was followed up by P. Ehrenfest, E. C. Kemble, M. Planck, tc. According to W. Burmeister, chlorine and bromine gases show no infra-red bsorption bands. This follows from P. Drude's hypothesis, for it is not to be xpected that the atoms in these otherwise symmetrical molecules should turn out bear charges of opposite sign; and the absence of these bands is considered to onfirm the view that the bands in this region are due wholly to atomic vibrations; nd that the presence of absorption bands is peculiar to those gases whose atoms re charged. Hydrogen bromide and chloride have each one double absorption and. No harmonics have yet been observed in the infra-red spectra of hydrogen romide and chloride; although E. C. Kemble anticipates that such may possibly e found if careful search be made.

Electrical conductivity.—According to A. L. Hughes and A. A. Dixon,[20] the **nizing potential** of hydrogen chloride gas representing the least energy required ionize the gas by the impact of electrons is 9·5 volts, when the value 6·56 volts furnished by K. T. Compton's formula $V=0\cdot194(K-1)^{-\frac{1}{2}}$ volt, where K is the pecific inductive capacity, and V the ionizing potential; the calculated value for ydrogen iodide is 4·55 volts. A. Reis gives for the energy of ionization of ydrogen chloride, bromide, and iodide, the respective values 326, 315, and 305 grm. cals.

Liquid hydrogen chloride, bromide, and iodide have a low electrical conuctivity.[21] The specific conductivity of liquid hydrogen chloride is $0\cdot167\times10^{-6}$ t its b.p.—a value not far from that of pure water. The specific conductivity of he liquid bromide is $0\cdot05\times10^{-6}$; and of the iodide $0\cdot2\times10^{-6}$. Most chlorides o not dissolve in liquid hydrogen chloride, but stannic chloride in soln. does ot make any appreciable difference to the conductivity. E. H. Archibald found hat quite a number of organic compounds formed conducting soln. in liquid ydrogen chloride.

The electrical conductivities of soln. of a great many compounds in liquid hydrogen alides have been measured by E. H. Archibald and D. McIntosh. The conductivity is aised considerably by phosphoryl chloride. Sodium; sodium sulphide, borate, phosphate, itrate, thiosulphate, and arsenate; chromic anhydride; potassium nitrate, hydroxide, bromate, sulphide, bisulphate, and ferro- and ferri- cyanide; ammonium fluoride and arbonate; rubidium and cæsium chloride; magnesium sulphate; calcium fluoride;

strontium chloride; barium chloride, oxide, nitrate, and chromate; copper and zinc sulphates; mercuric, boron, aluminium, stannous, manganous, and ferric chlorides; aluminium, ferrous, nickel, and cadmium sulphates; carbon dioxide; phosphorus tribromide; lead dioxide, nitrate, and cyanide; and tartar emetic do not change the conductivity of the liquid halides very much. Many ethers, ketones, esters, nitriles, nitroso-compounds, cyanides, thiocyanates, and ammonium bases form conducting soln. Acetic, butyric, propionic, benzoic, toluic, and salicylic acids form conducting soln. in liquid hydrogen chloride or bromide. The soln. of acetic, butyric, and benzoic acids conduct better than in water. Formic, maleic, o-phthalic, and cinnamic acids conduct in liquid hydrogen chloride, not the bromide.

Soln. of various organic substances in liquid hydrogen compounds—hydrogen chloride, bromide, iodide, sulphide, and phosphide—are conductors of electricity, and it seems as if the non-ionizing solvents become conductors by reaction with the solute. L. S. Bagster and B. D. Steele found that dry soln. of hydrogen bromide in liquid sulphur dioxide are practically non-conducting, but the addition of water gave conducting soln. which gave off hydrogen at the cathode, and bromine at the anode, whilst water was carried from anode to cathode, and deposited there. It was assumed that the water and hydrogen bromide form an oxonium compound which was electrolytic in character. It was shown that if a simple hydrate is formed, the deposit of water at the cathode must be due to the loss of hydrogen bromide holding it in soln. L. S. Bagster and G. Cooling have shown that this hypothesis is untenable because no like deposit of water appears at the anode. They further showed that the reaction is probably:

$$H_2O+HBr \rightleftharpoons {}^{H}_{H}{>}O{<}^{H}_{Br}$$

The oxonium compound then ionizes $H_3OBr \rightleftharpoons H_3O^{\cdot}+Br'$, and the $H_3O^{\cdot}$-ion loses its charge at the cathode during electrolysis and forms hydrogen and water.

Dielectric constants.—The dielectric constant of liquid hydrogen chloride [22] is 8·85 at −90° and 4·60 at 27·7° under the press. of its own vapour, and decreases still more with a rise of temp.—the temp. coeff. is about −0·8 per cent. Liquid hydrogen bromide has the value 6·29 at −80°, and 3·82 at 247°—the temp. coeff. is about −0·6 per cent. Liquid hydrogen iodide at −50° has the value 2·88, and at 21·7°, 2·90—the temp. coeff. is nearly zero. The dielectric capacity increases on solidification, for the solid, at −70°, had a dielectric constant of 2·95. Hence, the dielectric constants of the hydrogen halides increase with increasing mol. wt. The dielectric constants of these solvents are low in comparison with those of other solvents with a similar good ionizing power. The close parallelism shown by J. J. Thomson and W. Nernst, to subsist between the ionizing power and the dielectric constant of a solvent, and the fact that B. D. Steele, D. McIntosh, and E. H. Archibald have shown that the liquid hydrogen halides form good conducting soln. with several organic acids and alcohols, indicates that these solvents would have a high or medium dielectric capacity. The results show that the hydrogen halides have anomalously low values, meaning that unless the mobilities of the ions are abnormally high in these solvents, the parallelism with the dielectric capacity—if valid—is obscured by some other important factor. It is important to note that many organic solutes form compounds with the liquid halides—e.g. ether and hydrogen bromide form a compound $(C_2H_5)_2O.HBr$, melting at −42°; presumably

$$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}{>}O{<}\begin{matrix}H\\Br\end{matrix}$$

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§ 10. Properties of Hydrochloric, Hydrobromic, and Hydriodic Acids

Hydrogen chloride, bromide, and iodide are copiously soluble in water. Under atm. press. one volume of water absorbs 505 vols. of hydrogen chloride at 0° (H. Deicke, 1863); approximately 600 vols. of hydrogen bromide at 0° (M. Berthelot, 1873); and 425 vols. of hydrogen iodide at 10° (J. L. Gay Lussac, 1814). The absorption of the gases is accompanied by the evolution of much heat. The great solubility of hydrogen chloride is illustrated by the well-known experiment in which a large flask is filled with the gas and closed by a rubber stopper fitted with a glass tube drawn to a jet, so that the jet is 8 or 10 cm. from the bottom. The flask is inverted and the open end of the tube dipped in water tinted with blue litmus. The water rises in the tnbe as it absorbs the gas, and when it reaches the jet, it forms a water cascade or fountain inside the flask. At the same time, the blue litmus is coloured red, because the soln. of the gas in water is an acid—variously called *hydrochloric acid*, *chlorohydric acid*, *muriatic acid*, or *spirit of salts*. Similar remarks apply to the relations between hydrogen bromide and *hydrobromic acid*, or *bromohydric acid*, and between hydrogen iodide and *hydriodic acid* or *iodohydric acid*.

Solubility in water.—The solubility of hydrogen chloride in water at different temp. and press. has been investigated by H. E. Roscoe and W. Dittmar,[1] who found results which may be expressed in several different ways (press. 760 mm.). Let C denote the volumes of gas in c.c. per 100 c.c. of water; C_1 grms. of HCl per 100 grms. of water; and C_2 grms. of HCl per 100 grms. of soln.

	0°	4°	8°	12°	20°	30°	40°	50°	60°
C . . .	525·2	497·7	480·3	471·3	444·5	—	—	—	—
C_1 . . .	82·31	79·73	78·03	76·30	72·46	67·3	63·3	59·6	56·1
C_2 . . .	45·15	44·36	43·83	43·28	42·02	40·23	38·68	37·34	35·94

At temp. below 0° H. W. B. Roozeboom measured the amount of gas in grams dissolved by 100 grms. of water when the sum of the partial press. of hydrogen chloride and water was 760 mm. at the indicated temp.:

	0°	−5°	−10°	−15°	−18°	−18·3°	−21°	−24°
Grms. gas .	84·2	86·8	89·8	93·3	95·7	96·0	98·3	101·2

The soln. below −18·3 are supersaturated and unstable since there is a maximum in the solubility curve at −18·3° corresponding with the formation of the dihydrate, $HCl.2H_2O$, as indicated in Fig. 14.

Trihydrated hydrogen chloride, $HCl.3H_2O$, melting at −244°, is stated by S. U. Pickering to separate from soln. containing between 25·1 and 42·5 per cent. of hydrogen chloride at temp. between −80° and −25·65°. **Dihydrated hydrogen chloride,** $HCl.2H_2O$, separates when a sat. soln. of hydrogen chloride is cooled below −40°, and from soln. containing between 43·93 and 48·81 per cent. of HCl, at temp. between −26·25° and −17·5°. J. I. Pierre and E. Puchet[2] also obtained the same hydrate by leading dry hydrogen chloride into conc. hydrochloric acid cooled between −25° and 30°. This hydrate melts at 0°; and in open vessels dissociates at about −18·3°; in closed vessels at −17·7°. The heat of formation

of the solid hydrate is 14·1 Cals., and of the liquid 11·6 Cals. **Monohydrated hydrogen chloride,** $HCl.H_2O$, isolated by F. F. Rupert, has a sp. gr. 1·48, melts at −15·35°, and the vap. press. at the m.p. is 17·3 atm. The dihydrate is very soluble in water and sparingly soluble in liquid hydrogen chloride. The f.p. of the binary system, water and hydrogen chloride, have been determined for soln. containing less than 67 per cent. of hydrogen chloride, as shown in Fig. 13, by J. I. Pierre and E. Puchet, S. U. Pickering, H. W. B. Roozeboom, and F. F. Rupert (1909). Starting with pure water, the addition of hydrogen chloride steadily depresses the f.p. to the eutectic temp. −85°, *AB*, when the soln. contains 25 per cent. of HCl. Further additions of hydrogen chloride raise the freezing temp., *BC*, up to −24·4°, when the mixture contains 40·3 per cent. of HCl, and thus corresponds with trihydrated hydrogen chloride, $HCl.3H_2O$. Continued additions of hydrogen chloride depress the f.p. curve, *CD*, to a second eutectic, −28°, and then raise it, *DE*, to a second maximum, −17·7°, corresponding with 50·31 per cent. of HCl, that is, with dihydrated hydrogen chloride, $HCl.2H_2O$. The curve *EJ* represents the soln. in equilibrium with the gas at atm. press. S. U. Pickering did *not obtain the maximum with the dihydrate because its dissociation press. exceeds* 760 mm., and for the further exploitation of the system it is necessary to work in closed tubes. H. W. B. Roozeboom found the dissociation press. *p* mm. of mercury at different temp. to be

	−23·4°	−20·5°	−18·8°	−18·3°	−18·05°	−17·7°
p	194	376	628	760	893	1080 mm.

The sp. gr. of the dihydrate at −18·3°, referred to water at 4° is 1·46; and according to M. Berthelot, the heat of formation of the solid hydrate is 14·1 Cals. The f.p. curve again descends, *EF*, to a third eutectic, −23·5°, with increasing conc., and rises, *FG*, to a third maximum, −15·35°, when the soln. contains 66·9 per cent. of HCl, corresponding with monohydrated hydrogen chloride, $HCl.H_2O$. The first eutectic is concerned with the system, $H_2O : HCl.3H_2O$; the second *eutectic with the two hydrates,* $HCl.3H_2O$: $HCl.2H_2O$; and the third eutectic with the system, $HCl.2H_2O : HCl.H_2O$. Each of these three systems behaves like ice and brine. The three maxima thus correspond with the three hydrates, $HCl.3H_2O$; $HCl.2H_2O$; $HCl.H_2O$. All three hydrates have been isolated in the form of white crystalline solids. With more conc. soln. the liquid separates into two layers on cooling. The lighter liquid is almost pure hydrogen chloride with very little dissolved water. Soln. with between 67 and 99 per cent. hydrogen chloride do not exist at low temp. The solubility of water in liquid hydrogen chloride, *LK*, is less than 0·1 per cent. at 0°, and at the most 0·2 per cent. at 30°. The lower aq. layer, *GH*, represents soln. of liquid hydrogen chloride in water, which decreases with rise of temp.:

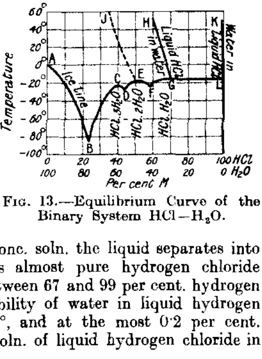

FIG. 13.—Equilibrium Curve of the Binary System $HCl-H_2O$.

	−15°	−5°	0°	5°	10°	20°	30°	40°	50°
HCl .	67·3	66·4	65·9	65·5	65·2	64·2	63·2	62·3	61·6 per cent.

Below −15°, the aq. layer freezes to crystals of the monohydrate. The solubility curves *HG* and *LK* do not approach a critical soln. temp. with rising temp.; at 54·5°, the HCl layer vanishes, on account of its proximity to the critical temp. of hydrogen chloride. The curve *LM* represents the solubility of the monohydrate in liquid hydrogen chloride. The existence of an octohydrate, $HCl.8H_2O$, has been inferred from the heat of soln. of hydrogen chloride in water; but it is quite an imaginary hydrate, for it has not been isolated. If it does exist, its presence is not

indicated on the f.p. curve, Fig. 13. Maximal points in a f.p. curve of a binary mixture thus represent compounds, minimal points eutectic mixtures. **The freezing or melting point curve of a mixture of two (or more) substances is often sensitive enough to demonstrate the existence of the more stable compounds, but it is too rough and inaccurate for the less stable compounds,** and there are compounds stable outside the range of the conditions represented by the curve. *For example, several definite compounds of phosphorus with sulphur or selenium* have been prepared which are not represented on the f.p. curves. Nevertheless, this method of investigating stable hydrates has been applied to ammonia, ferric *chloride hydrates, perchloric acid, sulphuric acid, nitric acid,* etc., and it has important application in metallurgy. G. Baume and co-workers also studied the binary systems: HCl and H_2S; HCl and C_2H_6; HCl and $C_2H_5.COOH$; HCl and CH_3OH; HCl and SO_2; and HCl and CH_3Cl.

J. Kendall, J. E. Booze, and J. C. Andrews[3] have shown that the formation of hydrates, in the sense of water of crystallization, with the weak acids very seldom occurs, and when hydrates are formed, the acid has the amphoteric character of a phenol. There is also a regular increase in the tendency of an acid to form hydrates, as the strength of the acid increases, until, with the strong acids, well-defined stable hydrates appear. The complexity and stability of the hydrates increase with the strength of the acid. These facts are in harmony with the weak acid nature of water.

The solubility curves of hydrogen bromide have been investigated by H. W. B. Roozeboom and S. U. Pickering.[4] The absorption coeff. *B* is indicated below. H. W. B. Roozeboom gives for the number of grams of hydrogen bromide *C* per 100 grms. of soln., or C_1 per 100 grms. of water, between 760 and 765 mm. press.:

	−20°	−10°	0°	10°	25°	50°	75°	100°
B	—	—	611·6	581·4	532·1	468·6	406·7	344·6
C	247·5	233·5	221·2	210·3	193·0	171·5	150·5	130·0
C_1	—	—	68·85	67·76	65·88	63·16	60·08	56·52

The solubility with ice as the phase ranges from 35·755 per cent. of HBr at −64·8° to 3·490 per cent. of HBr at −1·5°. The solubility with the tetrahydrate as the solid phase ranges from 54·772 per cent. of HBr at −56·8° to 47·069 at −66·5°; and with the trihydrate as the solid phase from 59·517 per cent. of HBr at −47·9° to 47·9° to 55·699 at −54·0°. These solubility curves are eq. to the f.p. curves shown in Fig. 14. The hydrates of hydrogen bromide are therefore **monohydrated hydrogen bromide,** $HBr.H_2O$, stable between −3·3° and −15·5°, and between 1 and 2½ atm. press., and in soln. containing between 1·21 to 1·64 mol. of water to a mol. of hydrogen bromide. Outside one extreme of these limits liquid hydrogen bromide appears, and outside the other, the dihydrate. The m.p. of the dihydrate has not been observed. **Dihydrated hydrogen bromide,** $HBr.2H_2O$, is stable between −15·5° and −11·3°; and between −11·3° and −47·9°, at about 2½ atm. press., *and in soln. containing* 1·64 *to* 3·05 *mol. of hydrogen bromide to one of* water. The solid phases outside the extreme limits are the di- and tri- hydrates. The dihydrate forms white crystals of sp. gr. 2·11 (−15°). According to H. W. B. Roozeboom, its heat of formation at −15° is 16·92 Cals. M. Berthelot's values 14·2 Cals. refers to the heat of formation of the liquid. **Trihydrated hydrogen bromide,** $HBr.3H_2O$, is stable between 47·9° and −36·8°, in soln. containing from 3·05 to 3·71 mol. of water to one of the bromide. The extrapolated m.p. is −47·5°, and the two solid phases outside the extreme limits are the di- and tetra- hydrates. **Tetrahydrated**

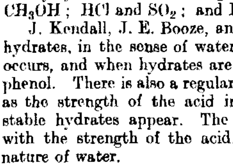

FIG. 14.—Equilibrium Curve of the Binary System $HBr-H_2O$.

hydrogen bromide, $HBr.4H_2O$, is stable at about $-55·8°$ or $-56·8°$ in soln. containing about 3·71 mol. of the bromide. Its m.p. is $-55·8°$. S. U. Pickering also assumed the formation of *pentahydrated hydrogen bromide*, $HBr.5H_2O$, but there is some doubt about the existence of this compound. G. Baume and N. Georgitses also studied the binary system HBr and H_2S.

The solubility curve of hydrogen iodide [5] is indicated in Fig. 15, which also represents the f.p. curve. Since the quantity of absorbed gas changed very little with variations of temp., M. Berthelot concluded that hydrates must be formed in aq. soln., and S. U. Pickering investigated the f.p. and saturation curves in the system: hydrogen iodide and water. He showed the existence of the three hydrates indicated in the diagram by passing hydrogen iodide into hydriodic acid cooled by a freezing mixture, (i) a mass of crystals of **dihydrated hydrogen iodide**, $HI.2H_2O$, melting at about $-43°$; (ii) small granular crystals of **trihydrated hydrogen iodide**, $HI.3H_2O$, melting at about $-48°$; and (iii) large crystals of **tetrahydrated hydrogen iodide**, $HI.4H_2O$, melting at about $-36·5°$. M. Berthelot's $HI.4·7H_2O$ is probably the imperfectly dried tetrahydrate.

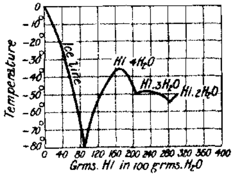

FIG. 15.—Equilibrium Curve of the Binary System H_2O-HI.

The effect of press. on the solubility of hydrogen chloride was determined by H. E. Roscoe and W. Dittmar. In the first case, the indicated press. in mm. of mercury were obtained by subtracting the vapour press. of water from the observed press. The amounts of hydrogen chloride in grams dissolved by 100 grms. of water at different press., and at 0°, are:

	60	100	200	400	500	750	1000	1300 mm.
Grams HCl .	61·3	65·7	70·7	76·3	80·0	82·4	85·6	89·5

The solubility of the gas does not follow Henry's rule: the amount of gas dissolved at a constant temp. varies proportionally with the press. If it did, since 100 grms. of water dissolve 89·5 grms. of the gas at 1000 mm. press., the solubility at one-tenth this press., *viz.* at 100 mm. press., should be one-tenth this amount, *viz.* 8·95 grms., whereas the actual amount dissolved is 65·7 grms. This behaviour of the gas, says H. E. Roscoe and W. Dittmar, renders it necessary to assume that there is a powerful attraction of the nature of chemical affinity between the molecules of water and of the gas, and which is different from the attractive force between the molecules of the water and the molecules of other gases which follow Henry's rule. According to the ionic hypothesis, it is assumed that the greater portion of the dissolved gas is ionized, and that only the smaller portion which is not ionized follows Henry's rule. H. W. B. Roozeboom found similarly at temp. below 0°, the amount of gas in grams dissolved by 100 grms. of water at press. above and below 760 mm. is 86·8 grms. at $-21°$ and 334 mm. press.; 92·6 grms. at $-19°$ and 580 mm.; 98·4 grms. at $-18°$ and 900 mm.; and 101·4 grms. at $-17·7°$ and 1073 mm.

As in the case of hydrogen chloride, the effect of press. on the solubility of hydrogen bromide in water is not in accord with Henry's law. Thus, H. W. B. Roozeboom found that at 0°, a gram of hydrogen bromide at 5 mm. press.; 2·504 at 380 mm.; 2·116 at 540 mm.; and 2·212 at 760 mm. press. He also examined the press.-temp. concentration curves.

The specific gravity and concentration.—The sp. gr. of aq. soln. of hydrogen chloride of various conc. have been determined by J. Kolb, J. C. G. de Marignac, G. Lunge, etc.[6] G. Lunge's results are indicated in Table VI for various conc. of the acid at 15°; water at 4° unity.

TABLE VI.—SPECIFIC GRAVITIES OF HYDROCHLORIC ACID OF DIFFERENT CONCENTRATIONS.

Specific gravity at 15° in vacuo.	100 parts by weight correspond to parts by weight of HCl.	1 litre contains g. of HCl.	Specific gravity at 15° in vacuo.	100 parts by weight correspond to parts by weight of HCl.	1 litre contains g. of HCl.
1·000	0·16	1·6	1·105	20·97	232
1·005	1·15	12	1·110	21·92	243
1·010	2·14	22	1·115	22·86	255
1·015	3·12	32	1·120	23·82	267
1·020	4·13	42	1·125	24·78	278
1·025	5·15	53	1·130	25·75	291
1·030	6·15	64	1·135	26·70	303
1·035	7·15	74	1·140	27·66	315
1·040	8·16	85	1·145	28·61	328
1·045	9·16	96	1·150	29·57	340
1·050	10·17	107	1·155	30·55	353
1·055	11·18	118	1·160	31·52	366
1·060	12·19	129	1·165	32·49	379
1·065	13·19	141	1·170	33·46	392
1·070	14·17	152	1·175	34·42	404
1·075	15·16	163	1·180	35·39	418
1·080	16·15	174	1·185	36·31	430
1·085	17·13	186	1·190	37·23	443
1·090	18·11	197	1·195	38·16	456
1·095	19·06	209	1·200	39·11	469
1·100	20·01	220			

The percentage composition p of a soln. of sp. gr. D is nearly $p=200(D-1)$. J. Thomsen based the formula

$$\text{Specific gravity, } D=\frac{100}{100-p}\left(\frac{100-1\cdot0765p}{100-0\cdot726p}\right)^3$$

for the relation between the sp. gr. D and the amount of hydrogen chloride p in grams in 100 grms. of soln. upon some old sp. gr. tables of A. Ure. H. Gautier has shown that the amount of hydrogen chloride in grams in 100 grms. of soln. is given approximately by dividing the sp. gr. less unity by 5·1. The sp. gr. of soln. of hydrogen bromide of different concentrations [7] is indicated in Table VII.

TABLE VII.—SPECIFIC GRAVITIES OF HYDROBROMIC ACID OF DIFFERENT CONCENTRATIONS.

Per cent. HBr.	0	1	2	3	4	5	6	7	8	9
0	—	1·007	1·014	1·021	1·028	1·035	1·043	1·050	1·058	1·065
1	1·073	1·081	1·089	1·097	1·106	1·114	1·122	1·131	1·140	1·149
2	1·158	1·167	1·176	1·186	1·196	1·206	1·215	1·225	1·235	1·246
3	1·257	1·268	1·279	1·290	1·302	1·314	1·326	1·358	1·351	1·363
4	1·376	1·389	1·403	1·417	1·431	1·445	1·459	1·475	1·487	1·502

The sp. gr. of soln. of hydrogen iodide sat. at atm. press. is 1·99 or 2·00, and it fumes in air. The sp. gr. of different concentrations,[8] between 12° and 14°, is indicated in Table VIII, where the numbers are referred to water at the same temp. The sp. gr. of hydrobromic or hydriodic acid does not increase proportionally with the conc. The numbers by different observers are not very concordant.

TABLE VIII.—SPECIFIC GRAVITIES OF HYDRIODIC ACID OF DIFFERENT CONCENTRATIONS.

Per cent. of HI.	0	1	2	3	4	5	6	7	8	9
0	—	1·007	1·015	1·022	1·030	1·037	1·044	1·052	1·059	1·065
1	1·072	1·081	1·090	1·100	1·109	1·118	1·127	1·137	1·147	1·157
2	1·167	1·177	1·188	1·199	1·210	1·221	1·231	1·242	1·252	1·263
3	1·273	1·284	1·295	1·306	1·318	1·330	1·343	1·359	1·370	1·388
4	1·406	1·419	1·432	1·445	1·470	1·485	1·490	1·506	1·523	1·539
5	1·567	1·586	1·600	1·614	1·629	1·649	1·668	1·689	—	—

The **molecular volume,** v, of hydrochloric acid [9] containing n mol. of water is given as $v=18n+10n^{-1}$. The mol. vol. of dil. soln. of hydrogen chloride were found by F. Kohlrausch and W. Hallwachs to increase regularly with the molecular concentration. According to M. Berthelot and W. Louguinine, the mol. vol., v, of soln. of hydrogen bromide, $HBr+nH_2O$, is $v=18n+7n^{-1}+25·5$; and of hydrogen iodide, $HI+nH_2O$, is $v=18n+18·5$.

Coefficient of thermal expansion.—According to J. Kolb, the coeff. of thermal expansion of the conc. 43·09 per cent. acid is 0·058, nine times greater than that of water, while with ordinary—36·6 per cent.—acid, the coeff. is eight times larger than water. J. C. G. de Marignac found that if n denotes number of mol. of water per mol. of hydrogen chloride, θ the temp., α the coeff. of thermal expansion, and D the sp. gr. when the sp. gr. of water is 0·99826:

TABLE IX.

n	D	D at 20°	α	α at 20°
5·25	$1·13040-0·0_3 5049\theta+0·0_5 0005\theta^2$	1·12030	$0·0_3 4460+0·0_5 0430\theta$	$0·0_3 4546$
12·5	$1·07367-0·0_3 3001\theta-0·0_5 1666\theta^2$	1·06700	$0·0_3 2800+0·0_5 3301\theta$	$0·0_3 3460$
25	$1·03946-0·0_3 1580\theta-0·0_5 3253\theta^2$	1·03500	$0·0_3 1515+0·0_5 6418\theta$	$0·0_3 2799$
50	$1·02065-0·0_3 0673\theta-0·0_5 4378\theta^2$	1·01755	$0·0_3 0652+0·0_5 8710\theta$	$0·0_3 2394$
100	$1·01071-0·0_3 0313\theta-0·0_5 4845\theta^2$	1·00815	$0·0_3 0284+0·0_5 9780\theta$	$0·0_3 2240$
200	$1·00560-0·0_3 0173\theta-0·0_5 4847\theta^2$	1·00330	$0·0_3 0153+0·0_5 9768\theta$	$0·0_3 2107$

G. Lunge and L. Marchlewsky found that between 13° and 17° the sp. gr. of hydrochloric acid, between 1·000 and 1·040, increases or decreases 0·002 per degree below or above the standard 15°; for an acid between 1·041 and 1·085, ±0·003; between 1·086 and 1·120, 0·004; between 1·121 and 1·155, 0·005; and between 1·156 and 1·200, 0·006. N. A. Tschernay found the volume, v, of hydrochloric acid at $\theta°$ to be for $HCl+6·25H_2O$, $v=1+0·0_3 4460\theta+0·0_5 2125\theta^2$; $HCl+12·5H_2O$, $v=1+0·0_3 2800\theta+0·0_5 1650\theta^2$; $HCl+25H_2O$, $v=1+0·0_3 1515\theta+0·0_5 3209\theta^2$; for $HCl+50H_2O$, $v=1+0·0_4 652\theta+0·0_5 4355\theta^2$. G. Tammann and Z. Kozarzewsky and N. A. Tschernay [10] found the maximum density of soln. with n mol. of hydrogen chloride per 1000 grms. of water, and the coeff. of thermal expansion α, at 20°, to be:

n . . .	0·41	0·94	1·71	2·01	2·99
Temp. . .	1·19°	−2·26°	−10·64°	−14·45°	−26·25°
α at 20° . .	0·00021	0·00023	0·00025	0·00025	—

The maximum density of a 1·98 per cent. soln. of hydrobromic acid is 2·30°. A litre flask of an approximately normal soln. of hydrochloric acid at 15° requires the addition or subtraction of the amounts in c.c. indicated in Table X, according as the temp. is above or below the standard 15°; and for one-tenth normal soln. or soln. of less concentration, the amounts indicated in Table XI.

TABLE X.—TEMPERATURE CORRECTION FOR N-HCl SOLUTIONS.

Temp.	0	1	2	3	4	5	6	7	8	9
0	—	—	—	—	—	+1·3	+1·2	+1·1	+1·0	+0·9
1	+0·8	+0·7	+0·5	+0·3	+0·2	Unit	−0·2	−0·4	−0·6	−0·8
2	−1·1	−1·3	−1·5	−1·8	−2·1	−2·3	−0·5	−2·8	−3·1	−3·4

TABLE XI.—REDUCTION FOR THE CHANGE OF THE APPARENT VOLUME OF A LITRE OF WATER WITH TEMPERATURE.

Temp.	0	1	2	3	4	5	6	7	8	9
0	—	—	—	—	—	+0·63	+0·63	+0·60	+0·57	+0·53
1	+0·48	+0·41	+0·32	+0·22	+0·12	Unit	−0·13	−0·28	−0·43	−0·60
2	−0·77	−0·96	−0·16	−1·37	−1·58	−1·81	−2·05	−2·30	−2·57	−2·82
3	−3·10	−3·38	−3·67	−3·97	−4·28	−4·60	−4·93	−5·27	−5·61	−5·96

According to W. H. Perkin,[11] the sp. gr. of a 42·7 per cent. soln. of hydriodic acid is 1·4537 at 10°; 1·4507 at 15°; 1·4484 at 20°; and 1·4467 at 25°.

Viscosity.—The viscosity,[12] η, of soln. of hydrochloric acid containing N mol. of HCl per litre, determined by W. H. Green at 24·9°, referred to water at 0° unity, and also in absolute units :

N . .	0	2	4	6	8	10	12
Relative, η .	1·0000	1·1234	1·2572	1·4108	1·6041	1·8432	2·1387
Absolute, η .	0·008977	0·010085	0·011286	0·0126650	0·0143990	0·016545	0·19198

At low temp. the viscosity increases very much. F. Dorn and B. Völlmer found the viscosity of the 24·3 per cent. acid to be 0·01635 at 15°, and at −79° approximately 0·9. According to R. Reyher, the viscosity η of normal hydrobromic acid at 25°, referred to water at 25°=unity, is 1·0320 ; and for soln. of concentration C, η=1·0378c. *According to F. Kohlrausch, at 18°, 5, 10, and 15 per cent. soln. have* respectively the viscosities 0·000637 ; 0·001318 ; and 0·002046.

Rate of diffusion.—The coeff. of diffusion of hydrogen chloride in aq. soln., determined by J. D. R. Scheffer[13] at 0°, is, for soln. containing N mol. of HCl per litre, in sq. cm. per day ;

N	4·23	3·28	2·43	1·775	0·962	0·210
Diffusion coeff. .	2·31	2·08	1·86	1·67	1·52	1·39

at 19·2°, and N=3·2, the coeff. is 3·89 ; and for N=0·02, 2·12 for hydrobromic acid in dil. soln. at 18°, the diffusion coeff. is 2·48 sq. cm. per day ; and for hydriodic acid, 2·46 sq. cm. per day. According to C. Umoff, the diffusion coeff. of hydrogen chloride is 490×10^{-7} sq. cm. per sec., and of hydrogen bromide 497×10^{-7} sq. cm. per sec. The velocities of diffusion of the three acids are related as 989 : 965 : 994.

The **compressibility** of soln. of 250 litres of gas in a litre of soln. is 0·0000366 at 20·5°. This is less than the value for water, and is considered by F. Isambert[14] to indicate that a compound is formed in the soln. W. C. Röntgen and J. Schneider measured the compressibility of hydrochloric and hydrobromic acids. They found for a 2·51 per cent. soln. at 17·5°, a compressibility of β=0·00004295 ; and of a 5·24 per cent. soln., 0·0000418. M. Schmidt found for a 36·7 per cent. soln. of the former acid, 0·0000377 at 15·8°. W. C. Röntgen and J. Schneider found the compressibility of a 10·77 per cent. soln. of hydrogen bromide at 17·72° is 0·00004419 ; and of a 5·23 per cent. soln. at 17·81° is 0·00004511.

Vapour pressure.—The partial press. of hydrogen chloride for aq. soln. of the gas has been measured by F. B. Allan[15] at 18·4°, by R. Gahl at 25°, and by F. Dolezalek at 30°. If C denotes the number of grams of hydrogen chloride per 1000 grms.

of the solvent at 25°, S. J. Bates and H. D. Kirschman found that the partial press., p, of hydrogen chloride, bromide, and iodide in mm. of mercury are:

C	4·0	5·0	6·0	7·0	8·0	9·0	10·0	11·0
p(HCl)	0·0182	0·0530	0·140	0·348	0·844	1·93	4·20	—
p(HBr)	—	—	0·00151	0·00370	0·0089	0·0226	0·059	0·151
p(HI)	—	—	0·00057	0·00182	0·0065	0·0295	0·132	—

According to F. Dolezalek, for 4·98N-HCl the partial press. of the hydrogen chloride is 0·24 mm., and for 12·25N-soln., 337 mm. If x denotes the number of mol. of hydrogen chloride divided by the number of mol. of water, the partial press. of the more conc. soln. of hydrogen chloride, p mm. at 30°, is given by $\log_{10} p=7{\cdot}9 \log_{10} x+6{\cdot}6421$. S. J. Bates and H. D. Kirschman found the **free energy** of the hydrogen halides in aq. soln. of n mols. per 1000 grms. of water at 25°

n	0·1	6·0	7·0	8·0	9·0	10·0
HCl	−34330	−27790	−27250	−26725	−26325	−25775 cals.
HBr	−27550	−20365	−19830	−19300	−18760	−18190 ,,
HI	−15260	−8035	−7360	−6600	−5700	−4815 ,,

According to H. W. B. Roozeboom, D. Konowaloff, and M. Bodenstein and A. Geiger, the vapour press. of soln. of hydrobromic acid with 2·056 grms. of HBr per gram of water is 10 cm. at −25°, and 38 cm. at 0°; for a soln. with 2·120 grms. of HBr for gram of water, 14 cm. at −25°, and 54 cm. at 0° with a soln. containing 2·116 grms. of HBr per gram of water. A soln. containing 2·268 grms. of HBr per gram of water has a vap. press. of 30 cm. at −25°, and 73 cm. at −5° when the soln. contains 2·264 grms. of HBr per gram of water.

The partial press. of hydriodic acid is very small on account of the affinity of the hydrogen iodide for water. According to P. Stegmüller, for soln. with 5·5 mols. of hydrogen iodide per litre, the partial press. of hydrogen iodide is 0·0000112 atm. at 31·6°; 0·0000873 atm. at 55·2° and 0·000661 at 81·6°; similarly, for a soln. with 4·62 mols. of hydrogen iodide per litre, the partial press. is 0·00000121 atm. at 31·6°; 0·0000107 atm. at 55·2°; and 0·0000964 atm. at 81·6°.

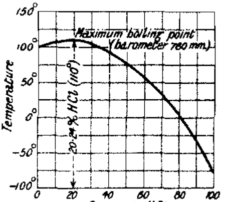

FIG. 16.—Boiling Points of Aqueous Solutions of Hydrogen Chloride.

Boiling points.—The effect of hydrogen chloride on the b.p. of water is illustrated by the curve, Fig. 16. The fact that the conc. acid becomes weaker and the dil. acid stronger when boiled was known to J. Dalton[16] in 1802, and the subject was investigated by A. Bineau in 1843, and by H. E. Roscoe and W. Dittmar in 1860. The latter showed that if an aq. soln. of hydrogen chloride containing more than 20·24 per cent. HCl be heated, hydrogen chloride with but little water is given off; the soln. becomes less conc.; the vap. press. of the soln. diminishes; and consequently, the b.p. rises as indicated by the curve. This continues until the soln. contains nearly 20·24 per cent. of HCl, when its b.p. attains a maximum value, 110°; any further boiling does not affect the concentration of the aq. soln. because dil. acid containing 20·24 per cent. of HCl distils unchanged. Again, if an acid containing less than 20·24 per cent. of HCl be boiled, water accompanied by a little hydrogen chloride passes off; the b.p. of the soln. gradually rises; and at the same time the soln. becomes more conc. until it contains 20·24 per cent. HCl, when the acid of constant b.p. distils over unchanged at 110°. Hence 110° is the maximum b.p. of hydrochloric acid at atm. press. Similar phenomena occur with nitric and with several other acids. A. Bineau thought that the acid which corresponded with the maximum b.p. was an octohydrate—that is, a chemical compound of hydrogen chloride and water—$HCl.8H_2O$; but H. E. Roscoe and W. Dittmar showed that

the composition of the constant boiling acid varies with the press., and since compounds *do not usually vary in composition* with changes of press., A. Bineau's hypothesis has been abandoned. For example, the composition of the constant boiling acid obtained at different press. varies from 23·2 per cent. hydrogen chloride with a press. of 50 mm. to a 18·0 per cent. acid with a press. of 2500 mm.

A. Bineau also showed that by conducting a stream of air through conc. hydrochloric acid, at 15°, the residue with a constant composition contains 25·2 per cent. hydrogen chloride corresponding with the hexahydrate, $HCl.6H_2O$. Conversely, *with a dil. acid, water is lost until the residue has the same composition.* In confirmation, T. Graham observed a special retardation in the rate of flow of hydrochloric acid of diminishing concentration through capillary tubes with an acid corresponding with $HCl.6H_2O$. and assumed that a definite hydrate was formed. H. E. Roscoe and W. Dittmar showed that at 0° the residue of constant composition *has 25·0 per cent. hydrogen chloride, and as the temp. rises, the acid of constant* composition has less and less hydrogen chloride, until, at 100°, it contains 20·7 per cent. of this gas in soln. H. E. Roscoe and W. Dittmar also showed that an aq. soln. of hydrogen chloride which remains unchanged, at a definite press., boils at a certain definite temp., and is identical with the soln. obtained by treatment with a stream of dry air under ordinary press. and the same temp. For example, a soln. with 22·8 per cent. of hydrogen chloride boils constantly between 61° and 62° at 100 mm. press., and a soln. of the same concentration is obtained by leading dry air through acid at 62°. With soln. of oxygen, ammonia, hydrogen, and nitrogen in water, the more volatile constituent leaves the soln. before all the boiling water has evaporated. Hydrochloric acid with the constant boiling composition evaporates as a mixture of water vapour and hydrogen chloride.

Fuming liquids.—*Soln. containing over 20 per cent. HCl fume in air.* Since conc. aq. soln. of hydrogen chloride have a vap. press. greater than water, we can see a reason for the fuming of hydrochloric acid in moist air; however conc. the acid, it does not fume in a bottle containing air dried by sulphuric acid. We know, of course, that hot water appears to fume in air because the cooler air in the vicinity of the hot water is *quickly sat. with water vapour.* Water at ordinary temp. does *not fume because it cannot give off more vapour than the air at the same temp. can* retain. Conc. hydrochloric acid fumes because the vapours which are given off unite with the aq. vap. in the atm. to form an acid with a smaller vap. press. than that of the conc. acid. Consequently, the air in the vicinity of the conc. acid is very quickly sat. with respect to the vapour of the new acid which is formed. The new acid, in consequence, condenses to minute globules of liquid which appear as mist. *Dilute* acids do not fume because any vapours which they give off do not form a liquid with a greater vapour press. than water. Hence, only those substances fume which give off vapours which unite with water to form a mixture or a compound with a vap. press. greater than water.

Hydrobromic and hydriodic acids behave in a similar manner. A. Bineau,[17] and P. Champion and H. Pellet found that constant boiling hydrobromic acid boils at 125° to 125·5° at 758 mm. press., and this acid has a sp. gr. 1·486, and contains 46·83 per cent. of hydrogen bromide. Hence A. Bineau thought it contained the pentahydrate $HBr.5H_2O$, but H. E. Roscoe showed that, as in the case of hydrochloric acid, the acid which boils constantly at 126° under a press. of 760 mm. and which has 47·86 per cent. of HBr, boils constantly at 153° under a press. of 1952 mm. and then contains 46·3 per cent. HBr. A. Bineau also found that in a desiccator over conc. sulphuric acid and potassium hydroxide, the residue contained 49·46 per cent. of HBr corresponding with $HBr.9H_2O$; the residue obtained on leading air through the acid at 16° contains 51·65 per cent. of HBr, and at 100°, 49·35 per cent. The most conc. acid has a sp. gr. 1·78, and contains 1·46 grms. HBr, or 82·02 per cent. HBr.

Constant boiling hydriodic acid[18] boils unchanged at 127°, 774 mm.; it has a sp. gr. 1·708; and contains 57·0 per cent. of hydrogen iodide. If dry air be passed

through the acid at 15°–19°, the residue contains 60·3 to 60·7 per cent. of HI; and at 100°, 58·2 to 58·5 per cent. of HI. A. Bineau regarded the constant boiling acid as a compound $2HI.11H_2O$, but as H. E. Roscoe proved, this acid is not a chemical individual. An acid with over 1·7 sp. gr. fumes in air. A soln. sat. at 0° has a sp. gr. 1·99.

Freezing points.—Numerous determinations[19] of the f.p. of hydrochloric acid have been made, and this acid has been regarded as a typical example for testing the deductions of the ionic hypothesis. The molecular lowering of the f.p., *i.e.* the quotient of the lowering of the f.p. by the mol. wt. rises from 2·52 for 0·00036*N*-soln. to a maximum of 3·680 with 0·003050*N*-soln.; it then falls to a minimum 3·546 with approximately 0·10*N*-soln., and slowly rises to 10·16 with 6·0*N*-soln. *For complete ionization, the molecular lowering of the f.p. should be* $2 \times 1·858 = 3·716$. Hence, the more dil. soln. are almost completely ionized, and the degree of ionization slowly decreases with increasing concentration. A. A. Noyes and K. G. Falk thus summarize the best representative values for 0·005*N*- to 0·10*N*-soln.:

N-soln. . .	0·005	0·01	0·02	0·05	0·10
Mol. lowering .	3·700	3·669	3·637	3·591	3·555
Ionization . .	99·1	97·5	95·7	93·3	91·7 per cent.

It is possible that the drop observed by H. Hausrath with soln. more dil. than 0·003*N*- is due to secondary disturbances. The fall from 0·003*N*- to about 0·2*N*-soln. is due to decreasing ionization, and the subsequent increase in the molecular lowering of the f.p. is thought to be due to the formation of hydrates. The f.p. curves of aq. soln. of the three haloid acids are shown in Figs. 13 to 15.

Heats of solution.—The heat of formation of a mol. of hydrogen chloride with the hydrogen and chlorine in dil. soln. is $H_{aq.}+Cl_{aq.}=HCl+39$ Cals. J. C. G. de Marignac represents the mol. ht. of formation, Q, of dil. soln. of hydrogen chloride, $HCl+nH_2O$, by the formula $Q=18n+11·65+140n^{-1}-268n^{-2}$; and H. Hammerl, for conc. soln., gives $Q=18n+28·93+151·3n^{-1}-242·1n^{-2}$. If a mol. of hydrogen chloride is dissolved in an excess, say, 200 to 300 mol. of water, the mol. ht. of soln. is 17·3 to 17·4 Cals.[20] The heat of soln. of hydrogen bromide: $HBr_{gas}+Aq.=HBr_{aq.}+19·9$ Cals. or 20·0 Cals.; the heat of formation of the acid: $H_{gas}+Br_{gas}+Aq.=HBr_{aq.}+32·0$ or 33·3 Cals.; $H_{gas}+Br_{liq.}=HBr_{aq.}+28·3$ or 29·6 Cals.; and further, $H_{gas}+Br_{aq.}=27·8$ or 19·1 Cals. Likewise with hydrogen iodide, $H_{gas}+I_{solid}+Aq.=HI+13·17$ Cals.; $H_{gas}+I_{solid}+Aq.=HI+20·686$ Cals. The heat of soln. is smaller if less water be present; thus, J. Thomsen found that if n denotes the number of mol. of water per mol. of hydrogen chloride, the heat of soln. of a mol. of the gas, at 18°, is

n . .	1	2	3	5	10	20	50	100	200
Heat soln.	5·375	11·365	13·362	14·959	16·157	16·756	17·115	17·235	17·315 cals.

M. Berthelot thinks the heats of dilution of hydrochloric acid favour the view that an octohydrate is formed, but this view is not generally accepted. H. von Steinwehr computed the heats of dilution of acids of different concentration. J. H. Ellis gave for the heats of dilution of $HCl+20H_2O$ to $HCl+nH_2O$, for $n=30$, 0·192 Cal.; $n=50$, 0·336 Cal.; $n=100$, 0·445 Cal.; $n=200$, 0·515 Cal.; $n=400$, 0·564 Cal.; $n=800$, 0·605 Cal.; and $n=2000$, 0·646 Cal. The heat evolved when a soln. $HCl+nH_2O$ is diluted to $200H_2O$ is, according to M. Berthelot, $Q=11620n^{-1}$ cals.; and when a soln. $HCl+nH_2O$ is diluted with mH_2O, $Q=11980\{n^{-1}-(n+m)^{-1}\}$. T. W. Richards found the heats of dilution from $HCl+8·8H_2O$ to $HCl+20H_2O$, and thence to $HCl+200H_2O$, to be respectively 0·556 and 1·330 Cals.; and E. Bose has shown that if a soln. contains x per cent. of water, the heat of soln. Q will be $Q=252·28808x-0·09894092x^2-0·006995567x^3$.

The heats of neutralization of eq. amounts of the hydroxides of the alkalies and alkaline earths, ammonium, magnesium, and thallium are between 12 and 14 Cals.;

for mercuric oxide, and zinc, cadmium, manganous, ferrous, cobaltous, nickelous, and aluminium hydroxides, between 9 and 11 Cals.; for lead and cupric oxide; cupric, ferric, and chromic hydroxide, between 5 and 8 Cals.; for mercurous oxide, 15 Cals.; and for silver oxide, 21 Cals. It is assumed that in the two last-named cases compounds are formed; that the acid and base and reaction products are wholly ionized when the heats of neutralization approximate 13·5 Cals.; and that ionization is only partial in the other cases.

The behaviour of hydrobromic and hydriodic acids is somewhat similar. The heat of soln., Q_s, of hydrogen bromide $HBr+nH_2O$; and the heats of dilution, Q_d, of $HBr.nH_2O$ to $HBr+200H_2O$ at 15°, when the results are expressed in Cals., is

n	0	2	3	4	5	6	7	8	10
Q_s	0	13·92	16·15	17·3	17·9	18·4	18·8	18·9	19·0
Q_d	20·0	0·08	3·85	2·7	2·1	1·6	1·2	1·1	1·0

Similarly, for hydrogen iodide, at 17°,

n	2	3	5	10	20	50	100	500
Q_s	12·54	14·81	17·38	18·58	18·99	19·14	19·18	19·21
Q_d	6·67	4·40	1·83	0·633	0·22	0·07	0·03	—

G. N. Lewis and H. Storch measured the free energy of dilution of hydrobromic acid from a concentration of $0·10N$- and $0·03N$-HBr to a concentration of $0·01N$-HBr to be respectively −2·582 Cals. and −1·239 Cals. For very dil. soln. of hydrogen bromide, the heat of soln., Q, according to E. Bose, is $Q=643·34335x-7·344342x^2-7·344342x^2+0·02919380x^3$, where x denotes the weight per cent. of water; similarly, for dil. soln. of hydrogen iodide, $Q=760·4683x-10·130416x^2+0·04474913 6x^3$. It will be observed that while the heat of soln. of hydrogen chloride is 17·3 Cals., the corresponding values for the bromide and iodide are nearly the same, being respectively 19·936 and 19·207 Cals. M. Berthelot's formula for the heat of dilution Q for soln. of $HBr+nH_2O$ in a large quantity of water is $Q=12·06n^{-1}-0·29$ cals., and if n exceeds 40, the last term is dropped; and his value for the heat of dilution Q for soln. with $HI+nH_2O$ is $Q=11·74n^{-1}-500$ cals., and when n exceeds 20, the last term may be omitted.

Specific heat.—The sp. ht., C, of soln. of hydrochloric acid with n mol. of water per mol. of hydrogen chloride have been determined by J. Thomsen,[21] J. C. G. de Marignac, and H. Hammerl. The following are compiled from these data:

n	4·23	5·20	6·49	10	20	50	100	200
C	0·627	0·660	0·688	0·749	0·855	0·932	0·964	0·979

The sp. ht. of the acid is less than that of the contained water; due, according to G. Tammann, *to an increase of the internal press. K of the soln. by the dissolved gas.* For temp. between 15·9° and 20·1°, the sp. ht. of the soln. $HCl+200H_2O$ is 0·9814; of $HCl+100H_2O$, 0·9634; $HBr+100H_2O$, 0·9433; and of $HI+100H_2O$, 0·9213; the corresponding mol. ht. for the three last-named soln. are respectively 1771, 1776, and 1778 Cals., thus showing that the mol. ht. increases with the mol. wt. According to H. W. B. Roozeboom, the sp. ht., C, of aq. soln. of hydrobromic acid, $HBr+nH_2O$, are:

n	1·84	2·00	2·48	2·72	4·01	10	50	100	500
C	0·3827	0·3553	0·3524	0·3608	0·4340	0·6150	0·8876	0·9402	0·9688

According to G. Jäger,[22] the heat conductivity of hydrochloric acid referred to water at 100 is 72·6 for soln. with 38 per cent. of hydrogen chloride, 79·4 for 25 per cent. soln.; and 12·5 for 85·8 per cent. soln.

Optical constants.—The index of refraction of hydrochloric acid is directly proportional to the density of the soln. Thus, J. Crichton[23] found

Sp. gr.	1·055	1·087	1·121	1·146	1·177
Index of refraction	1·053	1·088	1·121	1·138	1·180

for conc. soln. μ=1·4071. The molecular refraction at 13·2°, by J. H. Gladstone and T. P. Dale's formula, and for the D-line is 14·57 and 14·44 for soln. containing respectively 0·025 and 1·204 grms. of hydrogen chloride per 100 grms.; and at 20° by H. A. Lorentz and L. Lorenz's formula:

Per cent. HCl	7·74	15·00	28·23
Index of refraction, μ	1·3508	1·3675	1·3988
Lorentz and Lorenz's constant	14·51	14·40	14·26

If μ_0 be the refractive index of water, and C the number of grams of hydrogen chloride per 100 c.c. of soln., $(\mu-\mu_0)/C$ is not constant, but decreases with increasing concentration, and increases from 0·002198 to 0·002466 in passing from the spectral lines A to H. H. Jahn found for a soln. containing 7·24 grms. of HCl per 100 c.c., μ_a=1·3472, μ_D=1·3493, and μ_β=1·3540; the corresponding numbers with soln. containing 3·637 grms. of HCl per 100 c.c. were 1·3393, 1·3413, and 1·3455.

According to J. H. Gladstone,[24] the molecular refraction of hydrogen bromide in aq. soln. is 20·63; the index of refraction for Na-light is 1·325. According to A. Heydweiller, hydriodic acid is the only acid whose specific refraction does not increase with increasing ionization.

According to J. Tyndall,[25] the **absorption spectrum** of hydrogen chloride shows that the heat rays are absorbed, and likewise also with hydrogen bromide more than with bromine. W. H. Julius found an absorption band with hydrogen chloride at 3·68μ; and K. Angström and W. Palmaer, at 3·41μ. W. F. Colby, and E. S. Imes have studied the infra-red absorption bands of hydrogen fluoride, chloride, and bromide. W. de W. Abney and E. R. Festing found very feeble absorption lines in the ultra-red spectrum of liquid hydrogen chloride at 732$\mu\mu$, 741$\mu\mu$, 845$\mu\mu$, 867$\mu\mu$, and 949$\mu\mu$, and beyond that there is complete absorption.

The **magnetic rotation of the plane of polarization** [26] for the D-line determined by W. H. Perkin and O. Schönrock increases with concentration up to about 5 per cent. HCl, and subsequently decreases:

Per cent. HCl	1·90	4·05	5·65	7·17	15·63	30·86	41·7
Mag. rotation	4·746	4·831	4·931	4·856	4·419	4·305	4·045

The molecular magnetic rotation of a 65·59 per cent. soln. of hydrogen bromide is 7·669 (16°–19°); of a 56 per cent. soln., 8·061 (22°); of a 39·71 per cent. soln., 8·415 (20°–22°); of a 24·6 per cent. soln., 8·547 (18°): and of a 15·47 (16·5°) soln., 8·519. Similarly, with hydrogen iodide, a 67·02 per cent. soln. has a molecular magnetic rotation of 17·769 (20°–22°): a 65·1 per cent. soln., 17·868 (16°–17°); a 61·97 per cent. soln., 18·117 (17°–18°); a 56·78 per cent. soln., 18·308 (21°–22°); a 42·7 per cent. soln., 18·403 (14°–16°); a 31·17 per cent. soln., 18·451 (15°–17°); and a 20·77 per cent. soln., 18·428 (19°–22°). The effect of ionization on the magnetic rotation of these acids has been studied by F. Schwers. According to W. H. Perkin, the magnetic rotation of hydrogen chloride in ethyl alcohol soln. is 3·365; in isoamyl alcohol, 3·286; and in water, 2·261. O. Schönrock found the magnetic rotation in non-aqueous solvents to decrease with increasing concentration.

The electrical conductivity.—The electrical conductivity of hydrochloric acid has been very frequently measured.[27] The eq. conductivities, λ, of N-soln. of hydrochloric acid at different temp., by A. A. Noyes, are indicated in Table XII. For more conc. soln., of normality N, at 18°, the molecular conductivity is:

N	0·5	1	2	3	4	5	7	10
λ	327	301	254	215	181·5	152·2	106·2	64·4

The degree of ionization $a=\lambda/\lambda_\infty$ is also indicated in Table IX, on the assumption that the mobility of the hydrogen ion is not greater at infinite dilution than at other dilutions. If the correction is made for the decrease in the mobility with dilution the degree of ionization will be reduced between 5 and 6 per cent. The uncertainty in the estimation of the degree of ionization not only turns on the change in the

nobilities of the ions by dilution, but there is a possibility of a hydration of the ions, and the formation of complexes. The constant K deduced from W. Ostwald's

TABLE XII.—MOLECULAR CONDUCTIVITIES AND DEGREE OF IONIZATION OF HYDROCHLORIC ACID AT DIFFERENT TEMPERATURES.

N	Molecular conductivity λ; and percentage ionization.									
	λ at 18°	a	λ at 100°	a	λ at 156°	a	λ at 218°	a	λ at 306°	a
0	379·0	—	850	—	1085	—	1265	—	1424	—
0·0005	375·2	99·0	835	98·2	1064	98·0	1241	98·2	—	—
0·002	373·6	98·5	826	97·2	1048	96·5	1217	96·0	1337	94
0·01	368·1	97·1	807	95·0	1016	93·6	1168	92·2	1162	82
0·08	353·0	93·2	762	89·7	946	87·2	1044	82·5	862	60
0·1	350·6	92·6	754	88·7	929	85·6	1006	79·5	—	—

dilution law showing the change of the degree of ionization with dilution v, namely, $a^2/(1-a)v=K$, as with other strong electrolytes, decreases with increasing dilution from 3·1 with normal soln. to 0·044 for 0·0005N-soln. The deviations also occur when the values of a are computed from the lowering of the f.p., as well as from the electrical conductivity. There is a slow decrease in the degree of ionization with rise of temp., and increase of concentration. The former is taken to show that the ionization must be an exothermal process. P. D. Foote and F. L. Mohler attempted to prove that if the hydrogen chloride molecule consists of a positively charged hydrogen atom and a negatively charged chlorine atom bonded together, the process of ionization simply involves a direct disruption of this bond; and the **work of ionization** of a mol. of hydrogen chloride is estimated at 14 volts.

The relative rise of conductivity with *temperature* is smaller at the higher than at the lower temp. The temp. coeff. of the specific conductivity K are referred by F. Kohlrausch to a formula of the type $\frac{1}{8}(K_{26}-K_{18})/K_{18}$ for temp. between 18° and 26° for soln. between 0·01N and 0·0159N. S. Arrhenius uses for 0·001N-soln. 0·0163; 0·01N-soln. 0·0158; 0·1N-soln. 0·0153; and for 0·5N-soln. 0·0152 for specific conductivities between 18° and 52°. Several formulæ of the type $K=a+b\theta+c\theta^2+\ldots$ have been proposed; $K=K_{18}\{1+a(\theta-18)+b(\theta-18)^2\}$ is due to C. Déguisne, here $a=0{\cdot}0166$, and $b=0{\cdot}0000092$ for 0·0001N-soln.; $a=0{\cdot}01642$, $b=0{\cdot}0000155$ for 0·001N-soln.; and $a=0{\cdot}01641$, $b=0{\cdot}0000173$ for 0·01N-soln. F. Körber, G. Tammann and A. Bogojawlensky, J. Fink, and I. Fanjung have measured the influence of *pressure* on the conductivity of hydrochloric acid. The conductivity steadily increases proportionally with the press. up to 300 atm., and slowly decreases at still higher press. The percentage decrease in the resistance, or the percentage increase in the conductivity at the indicated press. over that at one atm. press. is 2·11, 5·86, and 9·46 for 100, 300, and 500 atm. press. respectively, for 0·002N-soln.; and 1·94, 5·72, and 9·33 for 0·001N-soln.

The **transport number** of chloride ions in 0·002N-soln. of hydrogen chloride is 0·171 at 18°; 0·166 for 0·05N-soln. at 18°; and 0·155 for 0·977N-soln. at 20°. The mobility of the ions is 0·154 at 0°; 0·167 at 18°; and 0·183 at 30°. The relative velocities of migration of the halogen ions at 18° increases with increasing at. wt.; bromine (at. wt. 80), however, is exceptional in possessing a lower mobility than iodine (at. wt. 127). The migration numbers at 18° are fluorine, 46·6; chlorine, 65·4; bromine, 67·6; and iodine, 66·4; and at 25°, fluorine, 54·6; chlorine, 75·7; bromine, 78·2; and iodine, 76·8. These numbers are expressed in conductivity units. The absolute **velocities of the ions** under the influence of an electromotive force of one volt are obtained by multiplying these numbers by 0·000010354. Thus, for chlorine ion, the velocity is 0·000678 cm. per second.

The molecular conductivity, λ, of hydrobromic acid at 25°, according to W. Ostwald, at a dilution of one mol. HBr in v litres of water, is

v . . .	2	4	8	16	32	64	128	512	1024
λ . . .	364	377	385	301	398	402	405	406	405

At 18°, the specific conductivities, K, of 5, 10, and 15 per cent. soln., are respectively 0·1908, 0·3549, and 0·4940; and the temp. coeff. are 0·0152, 0·0152, and 0·0150. Similarly, for hydriodic acid,

v . . .	2	4	8	16	32	64	128	512	1024
λ . . .	364	376	384	391	397	402	405	406	404

The maximum between v=128 and 1024 is due to secondary causes. According to F. Kohlrausch, the specific conductivity, K, of hydrochloric acid containing p per cent. of HI, is $K=2{\cdot}6575p$. The temp. coeff. at 18° is 0·0157. S. Arrhenius computes the **heat of ionization** for $\frac{1}{10}N$-soln. at 35°, HCl, −1·080 Cal., and HBr, −1·617 Cal. W. Maitland showed that the electric potential of the cell $I_2Aq.|I|$ normal electrode, is −0·3415 volt at 25°, G. N. Lewis and M. Randall obtained −0·6183 volt; and for the free energy of formation of the iodide ion $\frac{1}{2}I_2=I'$, they give −12·304 Cals. at 25°. T. Swensson has measured the e.m.f. developed when one side of the cell Pt | HCl, HCl | Pt is illuminated by ultra-violet light, for the combination forms a **photo-sensitive cell.**

The **free energy** of formation of the hydrogen halides at ordinary temp. may be calculated from the e.m.f. and vap. press. measurements. The **electromotive force** of the cell H_2 (1 atm.) | n-HCl | Cl_2 (1 atm.) allows the free energy of a mol. of HCl to be calculated in a soln. with n mols. per litre. If this result be added to the free energy attending the compression of a mol. of HCl from the press. at which it is in equilibrium with the soln., to a press. of one atm., the free energy of formation of hydrogen chloride is obtained. The e.m.f. data have been determined by J. H. Ellis, and G. A. Linhart, at 25° from cells of the type H_2 (1 atm.) | N-HCl, Hg_2Cl_2 | Hg, over a considerable range of concentration. The former's values for the e.m.f., and the decrease of free energy in the cell reaction, and attending the transfer of a mol. of HCl from any concentration to 0·1N-HCl, are indicated in Table XIII.

TABLE XIII.—E.M.F. AND FREE ENERGY CHANGES OF H_2 | HCL | NORMAL ELECTRODE CELLS.

Grm. mols. HCl per 1000 grms. water.	E.M.F. of cells.			Free energy decrease in cell reaction—joules.		
	18°	25°	35°	18°	25°	35°
4·484	0·15759	0·15506	0·15124	30415	29927	29190
1·0381	0·27919	0·27802	0·27595	53884	53657	53257
0·50948	0·31912	0·31865	0·31765	61590	61500	61307
0·10040	0·39764	0·39884	0·40013	76745	76977	77224
0·01001	(0·5271)	(0·5302)	(0·5369)	101740	102330	103630
0·00333	—	(0·8040)	(0·8105)	—	155170	156430

The terms included in brackets and the succeeding terms are less reliable than the others. R. C. Tolman and A. L. Ferguson measured the e.m.f. of the same type of cell at 18°; F. Dolezalek measured the e.m.f. of hydrogen-chlorine cells with conc. hydrochloric acid at 30° as electrolyte. G. N. Lewis and H. Storch have measured the free energy of hydrogen bromide in 0·1N-soln.; and G. N. Lewis and M. Randall, that of hydrogen iodide. For HBr gas, at 25°, the latter give −12·592 Cals., and for HI gas, 310 cals.

The decrease in free energy attending the transfer of a mol. of HCl from a

soln. of any normality n to one at $\frac{1}{10}N$-, is $E\epsilon$, where E is the e.m.f. of a cell where *the change takes place, and ϵ is the value of a farad. The same free energy change is expressed by means of $RT \log_e (p/p_{0\cdot1})$, where p and $p_{0\cdot1}$ represent the vap. press. of hydrogen chloride above soln. of the respective normalities n and 0·1n. Consequently, $E\epsilon = RT \log_e (p/p_{0\cdot1})$. E is obtained* by subtracting the e.m.f. of a cell in which the concentration is n-normal from that of a similar cell where the concentration is 0·1N-normal. The free energies of the hydrogen halides in soln. at various concentrations C mols. per litre of water, at 25°, computed in cals., by S. J. Bates and H. D. Kirshmann, are

C . .	0·1	0·5	1·0	2·0	4·0	6·0	8·0	10·0	11
E(HCl) .	−34330	−32500	−31590	−30510	−29100	−27790	−26725	−25775	—
E(HBr) .	—	—	—	—	—	−20365	−19300	−18190	−17635
E(HI) .	—	—	—	—	—	−8035	−6600	−4815	—

The free energy increase when the press. rises from its value over a 0·1N-soln. to a press. of 1 atm. is $RT \log (760/0{\cdot}0000223) = 11630$ cals. Hence the free energy of formation of gaseous hydrogen chloride at 25° is $-34330-(-11630) = -22700$ cals.; the corresponding values for hydrogen bromide is −12592 cals.; and for hydrogen iodide +310 cals. H. S. Harned has also investigated the changes of free energy in the cell reaction $H_2 + 2HgCl = 2HCl + 2Hg$, etc., in the presence of potassium, sodium, and lithium chlorides.

Catalytic effects.—Within certain limits, the stimulating action exerted by the presence of hydrochloric acid upon the speed of inversion of cane sugar[28] is less the more dil. the acid. Thus, W. Ostwald found the velocity constant with a soln. containing a mol. of acid per 2 litres of soln. is 20·52; per 10 litres, 3·335; and per 100 litres, 0·3128. The action is favoured by the presence of neutral salts, and this the more, the lower the mol. wt. of the salt in the same family group of the periodic system. The temp. coeff. of the inversion is 17·92 at 100°, and 0·04104 at 25°. W. Ostwald, R. Höpke, and H. Trey have likewise studied the accelerating influence of the acid on the hydrolysis of methyl and ethyl acetates. Similar studies have been made by W. Ostwald and A. Villiers on the hydrolysis of methyl and ethyl acetates, calcium oxalate, and ethyl bromide and iodide.

The affinities of the acids deduced from their electrical conductivity, and their influence on the rates of hydrolysis of methyl acetate and of the inversion of cane sugar are nearly the same, as illustrated in Table XIV.

TABLE XIV.—THE AFFINITIES OF SOME ACIDS.

	Electrical conductivity.	Hydrolysis of methyl acetate.	Inversion of cane sugar.
Hydrochloric acid . . .	100·0	100·0	100·0
Hydrobromic acid . . .	101·0	98·0	100·0
Hydriodic acid . . .	100·0	96·3	—
Nitric acid	99·6	92·0	73·2
Sulphuric acid . . .	65·1	74·0	75·4
Acetic acid	0·42	0·35	0·4

The order of the electrical conductivities runs parallel with the order of the affinities of these acids. The **dielectric constant** of soln. of hydrochloric acid are usually greater than that of water; for example, for 0·001N-soln., the dielectric constant is 0·990 (water unity); for 0·002N-soln., 1·033; and for 0·01N-soln., 1·126. The dielectric constants are not proportional to the conductivities of the soln.

Solubility in non-aqueous solvents.—Hydrogen chloride dissolves in many other solvents besides water—*e.g.* it dissolves in hydrocarbons, alcohols, aldehydes, ketones, ethers, esters, formic acid, nitrobenzene, aniline, pyridine, hydrogen

cyanide, sulphur dioxide, etc. *The number of grams of hydrogen chloride dissolved by 100 grms. of a soln. in methyl and ethyl alcohols and in ether:*

	−10	0	10	20	30
Methyl alcohol	54·6	51·3	—	47·0	43·0
Ethyl alcohol	—	45·4	42·7	41·0	38·1
Ethyl ether	37·51	35·6	30·35	24·9	19·47

Benzene dissolves about 2 parts of hydrogen chloride per 100 c.c. of solvent at 18°. W. F. Timojeeff found the mol. ht. of soln. in methyl alcohol to be from 1·105 to 1·649 cals.; ethyl alcohol, 1·173 to 1·713 cals.; propyl alcohol, 1·068 to 1·921 cals.; and in isobutyl alcohol, 1·185 to 1·794 cals. J. Kablukoff showed that the soln. in methyl alcohol has the largest conductivity, and that the conductivity in benzene, nitrobenzene, and analogous solvents is very low. The soln. in ether has no acidic properties, for it does not act on marble, magnesium, or sodium. In many cases more or less combination probably occurs—particularly with the alcohols and ethers—F. Jüttner, for example, has shown that the behaviour of the ternary system, $H_2O-HCl-(C_2H_5)_2O$, is in accord with this assumption. In some cases, the depression of the f.p., and the electrical conductivity of the soln., leads to the view that the hydrogen chloride is associated, as H. Zanninovich Tessarin found to be the case with soln. in formic acid, and E. Beckmann and G. Lockemann with soln. in benzene and nitrobenzene; the molecular conductivity of such soln. decreases with increasing dilution. The presence of moisture in these solvents reduces the association and increases the conductivity. A 60 per cent. soln. in ethyl alcohol has three times the conductivity of sulphuric acid. A satisfactory explanation of the various phenomena connected with the ionization of alcoholic and other non-aq. soln. is still wanting. There is a parallelism between the electrical conductivity of aq. soln. of the acids—assumed on the ionic theory to be eq. to the degree of ionization—and their chemical activity, but this breaks down with soln. in non-aq. solvents. For example, F. Zecchini found that a soln. of hydrogen chloride in ether acts more quickly than a soln. in methyl or ethyl alcohol in spite of the greater electrical conductivity of the latter. Marble is attacked by an aq. soln. of hydrogen chloride about forty times as fast as by a methyl alcohol soln. while potassium carbonate is scarcely attacked at all. The effects are here complicated by the solubility and rate of diffusion of the products of the reaction in the solvent. If water is rigorously excluded, a soln. of the gas in anhydrous alcohol or benzene has scarcely any effect on silver nitrate, and H. E. Patten and L. Kahlenberg found that the chemical activity of soln. of hydrogen chloride in various solvents bears no relation to the electrical conductivity. Analogous observations have been made with non-aq. soln. of hydrogen bromide and iodide.

According to T. de Saussure (1814), charcoal absorbs about 85 times its own volume of hydrogen chloride at 12° and under a press. of 724 mm.; and according to P. A. Favre, charcoal absorbs about 165 c.c. of hydrogen chloride per gram, and 10·0 Cals. of heat are evolved per mol. of gas absorbed. The actual amount absorbed depends upon the nature of the charcoal.[29] G. Gore has observed the Pouillet effect with hydrochloric acid and silica.

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§ 11. The Chemical Properties of the Hydrogen Halides and the Corresponding Acids

All the halogens form compounds with hydrogen, and the readiness with which union occurs decreases as the at. wt. increases. The properties of the halogen acids and their salts show as striking a relationship as those of the elements themselves. This is illustrated in Table XV.

TABLE XV.—THE PROPERTIES OF THE HALOID ACIDS.

Property.	Hydrogen fluoride.	Hydrogen chloride.	Hydrogen bromide.	Hydrogen iodide.
Molecular weight	20	36·46	80·93	127·93
Boiling point	19·4°	−83·4°	−67·1°	−35·5° (4 atm.)
Melting point	−92·5°	−111·4	−88·1°	50·9°
Solubility in water	35·3	42	49	57%
Specific gravity sat. aq. sol.	1·15	1·21	1·49	1·70
Boiling point aq. sol.	111° (43%)	110° (20%)	126° (47%)	127° (57%)
Dissociates at	—	1500°	800°	180°
Heat of formation	+38·5 gas	+22·0 gas	+12·3 gas	+0·4 gas
Heat of formation of K salt	110·6	105·7	95·3	80·1 Cals.
Heat of neutralization, NaOH	68	57	57	57 Cals.
Potassium salt melts	885°	790°	750°	705°
Calcium salt melts	1330°	780°	760°	740°
Solubility Ag salt	181·8	0·016	0·00084	0·000028%
Solubility Ca salt	0·16	24·7	58·8	67·6%

The exceptional character of fluorine.—Fluorine has a little more individuality, so to speak, than the other three members of the family: (1) There are no compounds of oxygen and fluorine ; (2) Chlorine, bromine, and iodine or the haloid acids show no signs of the remarkable effect of hydrofluoric acid and of fluorine on silicon ; (3) The solubilities of the sulphates, nitrates, and chlorides of barium, strontium, calcium, and magnesium decrease with increasing at. wt. of the metal, while the solubilities of the hydroxides increase ; the solubilities of the iodides, bromides, and chlorides

of potassium decrease with increasing at. wt. of the halide. Similar remarks apply to the solubilities of corresponding salts of lead, silver, gold, etc. Fluorine, however, seems to behave quite differently from the regular variation exhibited by the other halides. The solubilities of mercury and silver fluoride, and the sparing solubilities of calcium, strontium, and barium fluorides are in marked contrast with the solubilities of the corresponding salts of the other halogens; (4) Hydrofluoric acid in aq. soln. appears to be dibasic, whereas the other halide acids are monobasic. The other acids also do not form compounds corresponding with potassium acid fluoride, KHF_2; (5) *Fluorine is probably tervalent in a few compounds, but it is usually univalent, and it does not show the same variable valency as the other halogens*; (6) *The readiness with which fluorine forms complex fluo-metal acids or acid-fluorides* is also a characteristic property; (7) The abnormally low electrical conductivity of hydrogen fluoride is in marked contrast with the high conductivity of the other three halide acids.

By passing a series of electric sparks through hydrogen chloride gas, W. Henry[1] found that about one-thirty-fifth of its volume was decomposed into its elementary constituents; while H. St. C. Deville found the inductive discharge decomposed but a small proportion of the gas as evidenced by a slight decrease in volume, and by the formation of a little mercurous chloride owing to the action of the chlorine on the mercury over which the gas was confined. H. Buff and A. W. von Hofmann decomposed the gas almost completely by an electrically heated iron wire—ferric chloride was formed, and only a trace of hydrogen chloride remained undecomposed. There is very little evidence of the decomposition of hydrogen chloride at temp. below 1500°, but H. St. C. Deville found that if heated to 1500° in his *tube chaud et froid*, the product formed silver and mercurous chlorides when brought in contact with silver amalgam. Similar remarks apply to the action of heat on a mixture of hydrogen chloride and oxygen or air.

According to A. J. Balard,[2] hydrogen bromide—alone or mixed with oxygen is not decomposed when passed through a red-hot tube or when a lighted taper is lowered into the mixture. P. Hautefeuille[3] found that the decomposition of hydrogen iodide can be detected at 180° by the pale violet tinge of the vapour, and the amount of decomposition increases as the temp. rises; the decomposition is the more marked, the higher the press., and it is favoured by the presence of finely divided platinum. According to M. Berthelot, a mixture of hydrogen bromide with one-fourth its volume of oxygen is transformed completely into bromine and steam when heated 10 hrs. between 500° and 550°. P. Hautefeuille found no decomposition with hydrogen bromide alone at 700°; but M. Bodenstein obtained between 0·3 and 0·9 per cent. by suddenly cooling a mixture of the two gases at about 700°. Bluish-violet vapours of iodine are formed when hydrogen iodide is sparked, and there is a contraction in volume due to the deposition of iodine on the walls of the tube. J. L. Gay Lussac also found that a mixture of hydrogen iodide and oxygen is completely decomposed when passed through a porcelain tube at a red heat; and M. Berthelot showed that a mixture of hydrogen iodide with one-fourth its volume of oxygen, burns with a red flame. The equilibrium condition of the hydrogen halides at different temp.—Table I—has already been discussed.

The decomposition of hydrochloric acid by electrolysis has been considered. A. Bartoli and G. Papasogli[4] have investigated the electrolysis of hydrobromic acid; and A. Riche that of hydriodic acid—some bromic and iodic acid are respectively formed during the electrolysis.

If a moist mixture of hydrogen chloride and **oxygen** be exposed to sunlight, it acquires a perceptibly greenish tinge owing to the formation of free chlorine; and in 1849, N. W. Fischer[5] noted that a piece of gold-leaf in a jar of the mixed gases was attacked by the chlorine. According to A. Richardson, the dry gas is stable under these conditions. A. Cöhn and A. Wassilejewa showed that hydrogen chloride is appreciably decomposed into hydrogen and chlorine by exposure in quartz tubes to ultra-violet light. Hydriodic acid is not appreciably decomposed by the β- or

γ-radiations from radium bromide, if oxygen be absent, but in the presence of oxyger the rate of decomposition is augmented, and the effect is less, the higher the temp As in the action of heat on the stability of the hydrogen compounds of the sam *family of elements, their stability towards light decreases as the at. wt. increase The ultra-violet light from a mercury quartz lamp is needed to decompose hydroger chloride, while under similar circumstances hydrogen bromide is rapidly and completely decomposed; ordinary blue and violet light decomposes hydrogen iodide.* A similar relationship is found in the sulphur family—hydrogen oxide, sulphide, selenide, and telluride.

According to L. l'Hôte, hydrochloric acid in white, black, yellow, or red glass bottles is decomposed in light, and the free chlorine can be detected by the smell. E. Murmann found the dil. acid is stable under these conditions. According to M. Berthelot, the presence of a trace of manganese or iron chloride facilitates the oxidation of the hydrochloric acid. A. Richardson[6] also found that a mixture of hydrogen chloride and oxygen is perfectly stable in light even in the presence of aq. vapour provided liquid water be absent. H. B. Dixon found that sulphur dioxide is not oxidized by oxygen in the presence of water *vapour* at 100°, although in the presence of *liquid* water, oxidation readily occurs. M. Berthelot could detect no sign of the decomposition of hydrogen bromide after exposing the gas in a glass tube for 50 days. If the gas be mixed with oxygen, A. Richardson found that no action occurs if the gases be dried, but a reaction does occur if the gases be moist.

Similar remarks apply to a dry mixture of hydrogen iodide and oxygen; gaseous hydrogen iodide is not altered in darkness, and in sunlight, the decomposition is slow; according to G. Lemoine, only 0·24 per cent. is decomposed after 10 days' exposure, and 0·80 after 32 days'. The decomposition occurs in blue and violet light but not in red and green light. Dil. or conc. aq. soln., said G. Lemoine, do not decompose in light or darkness if air be excluded. The amount of iodine liberated from a soln. of hydriodic acid or of acidified potassium iodide, by oxygen and light, gradually reaches a maximum and then falls to zero. H. J. M. Creighton found that the phenomenon cannot be explained by the evaporation of the iodine; 500 c.c. of an acidified soln. of potassium iodide absorbed about 25 litres of oxygen in 10 weeks, and neither iodine nor iodate could be detected in the soln., nor did strong reducing agents liberate any oxygen. He says "the nature of the product is still a mystery." C. Winther found that thin rapidly moving layers of a soln. of hydrogen iodide, when subjected at a constant press. to the joint action of oxygen and light, are oxidized very slowly at the beginning, but later, the reaction attains a constant velocity. The phenomenon is attributed to the auto-sensitizing action of the liberated iodine.

R. Böttger found that the presence of copper prevented hydriodic acid becoming brown in light, and decolorized the acid already brown. The cuprous iodide which is formed is insoluble in the acid. M. Bodenstein found the decomposition of hydrogen iodide to be unimolecular in light, and independent of the press.; and bimolecular at 300°–500°. W. N. Hartley found that hydrogen iodide, bromide, or iodide retards the fluorescence of quinine sulphate, and J. Pinnow noted that, in general, substances which are decomposed by light diminish the fluorescence of quinine sulphate, fluoresceine, etc., and the presence of fluorescent substances facilitates the decomposition of substances decomposed by light.

The affinity of the halogen hydrides for **hydrogen peroxide** varies as the affinity of the halogen for oxygen. If hydrogen peroxide is added to hydrogen iodide a vigorous reaction is attended by the separation of iodine; if the iodide be added to the peroxide, a more vigorous reaction occurs, the iodine is volatilized and a colourless liquid remains. With the other halogen acids the reaction is more vigorous when the peroxide is added to the acid. The haloid salts behave similarly, and accordingly it is inferred that hydrogen peroxide first liberates the free acid and then decomposes it. **Oxidizing agents** like nitric, nitrous, bromic, and persulphuric acids, molybdic

acid, ferric chloride, etc., react with hydriodic acid, oxidizing the hydrogen and liberating iodine. The amount of iron can be determined by titration with standard sodium thiosulphate soln., and the result sometimes enables a determination of the corresponding oxidizing agents to be made. thus the amount of ferric chloride in a given soln. is related stochiometrically with the liberated iodine by the equation: $2FeCl_3+2KI=2FeCl_2+2KCl+I_2$. According to J. Plotnikoff and N. P. Strachoff, if in the photochemical reaction the potassium iodide and hydrochloric acid be in excess, the reaction is of the first order. The iodine liberated in the reaction might be expected to play the part of a light filter and retard the reaction, because a layer of iodine soln. interposed between the light source and the reacting system acts in this manner. No such retardation occurs when the concentration of the iodine in the system has between 2·7 and 27 millinormality, although a soln. of this concentration stops the reaction if used as an external light filter. When the concentration of the iodine reaches 54 millinormality, there is a fall in the velocity of the system. The failure of iodine soln. to conform to Beer's law is explained by changes in the iodine complexes with dilution; and the failure of the liberated iodine to act as a retarding agent on the reaction is attributed to the formation of an iodine complex which acts as an autocatalyst, which is but slightly sensitive to light.

J. Plotnikoff has studied the oxidation of hydriodic acid—obtained by a soln. of potassium iodide and hydrochloric acid—in water charged with oxygen. If the potassium iodide and hydrochloric acid are in large excess, the consumption of oxygen gas in darkness is slow, and in accord with a unimolecular reaction; and if the potassium iodide and hydrochloric acid are present in limited quantity, the reaction is proportional to the concentration of the oxygen, to the two-thirds power of the concentration of the potassium iodide, and the four-thirds power of the concentration of the hydrochloric acid. The reaction in darkness is accelerated by a cupric salt or a mixture of a ferric and cupric salt; manganous and lead salts exert no appreciable catalytic action; the catalytic effect of nitrous acid is very marked even if the soln. contains but the eq. of 0·00000006*N*-HNO_2. The reaction is accelerated by exposure to the light from a mercury lamp, and that proportionally with the intensity of the light although the reacting system does not absorb these rays to any appreciable extent. Additions of uranyl sulphite, eosine, starch, and cupric sulphite retard the velocity of the reaction in light; in darkness, the last-named catalyst accelerates the reaction. J. Pinnow found the rate of oxidation of mixtures of sulphuric acid and potassium iodide increases proportionally with the concentration of the sulphuric acid in light, but not in darkness provided the concentration of the iodine does not exceed a gram per litre. The accelerating influence of light is most marked in dil. soln. The reaction is twice as fast in darkness and in light when the sulphuric acid is replaced by hydrochloric acid. Hydrogen peroxide does not decompose hydrochloric acid, but bromine is separated from hydrobromic acid at 100°, and G. Cavazzi proposed to separate bromides from chlorides by this reaction—the free bromine can be removed from the soln. by aspiration. L. J. Thénard showed that hydrogen iodide is oxidized by hydrogen peroxide with the separation of iodine, $H_2O_2+2HI=2H_2O+I_2$. The reaction is accelerated by hydrochloric and other acids, and the catalytic effect is assumed by G. Magnanini [7] to be proportional to the affinity constant of the acid. The reaction is also accelerated by ferrous sulphate, copper sulphate, tungstates, and molybdates.

Chlorine gas reacts with hydrogen bromide or iodide to form hydrogen chloride and the separation of the corresponding halogen, $2HX+XCl_2=2HCl+X_2$. The free halogen then combines with the excess of chlorine, forming bromine or iodine chloride. A little free chlorine turns hydriodic acid brown, and the colour is removed by an excess of chlorine. **Bromine** similarly displaces iodine from hydriodic acid. The halogen is also liberated by the action of hypochlorites or bleaching powder on bromides or iodides. **Hypochlorous acid** and hydrochloric acid give chlorine and water: $HOCl+HCl=H_2O+Cl_2$; **chloric acid** forms chlorine mono- and di-oxides and free chlorine in varying proportions. Two volumes of hydrogen chloride and one

volume of chlorine monoxide form one volume of steam and two volumes of chlorine: $Cl_2O+2HCl=H_2O+2Cl_2$. **Potassium chlorate** with an excess of hydrochloric acid reacts: $KClO_3+6HCl=KCl+3Cl_2+3H_2O$; **potassium bromate**; $2KBrO_3+12HCl=2KCl+Br_2+5Cl_2+6H_2O$, and **iodic acid**: $HIO_3+5HCl=ICl_3+Cl_2+3H_2O$, but there is no reaction with dil. soln.[8] Molten potassium chlorate inflames hydrogen iodide, a red flame appears and free iodine is formed. A. J. Balard found that an aq. soln. of iodic or **periodic acid** with hydriodic acid forms iodine and water. The reaction between bromic and hydriodic acids has been much investigated:[9] $6HI+HBrO_3=HBr+3H_2O+3I_2$. The hydrobromic acid formed in the reaction exerts a reducing action on the bromic acid: $5HBr+HBrO_3=3H_2O+3Br_2$, but about 58 times more slowly. The liberated iodine acts catalytically on the reactions retarding the speed of the reaction. O. Burchard also measured the velocity of the reaction of hydriodic acid on chloric and iodic acids. The reaction: $5HI+HIO_3=3H_2O+3I_2$, was also investigated by R. Luther and G. V. Sammet.

According to J. B. A. Dumas,[10] aq. soln. of **sulphur dioxide** are not decomposed by hydrochloric acid, but the dry gases, when confined over mercury, form water, chlorine, and sulphur: $4HCl+SO_2=2H_2O+S+2Cl_2$. E. Péchard found hydriodic acid absorbs sulphur dioxide forming an orange-yellow soln. from which free iodine is absent; and compounds of sulphur dioxide with the iodides of the alkali and alkaline earth metals have been reported. Selenium and tellurium dioxides, according to A. Ditte, absorb dry hydrogen chloride forming addition products—*e.g.* $SeO_2.HCl$; $SeO_2.2HCl$; TeO_2HCl; and $2TeO_2.3HCl$. J. B. A. Dumas also noted that sulphur dioxide and hydrogen iodide form sulphur, iodine, and water: $SO_2+4HI=2H_2O+S+2I_2$; when the two gases meet, there is a deep red flash, and the sides of the containing vessel are immediately covered with crystals of iodine. E. Soubeiran says there is no action if the gases be quite dry. The two gases in aq. soln. react forming a yellow precipitate, and this the more the more conc. the soln. **Sulphur** and **selenium,** according to P. Hautefeuille, decompose hydrogen iodide at ordinary temp., and conc. hydriodic acid when heated; and M. Berthelot says that dry hydrogen iodide and sulphur react in the cold, more rapidly at 100°, and still more rapidly at 500°, $2HI+S=H_2S+SI_2$. A. E. Menke also supposed sulphur iodide was formed when sulphurous and hydrochloric acids react together. The real product appears to be a solid soln. of iodine and sulphur. According to G. Aimé, **sulphur trioxide** absorbs hydrogen chloride, forming a liquid—chlorosulphonic acid. Gaseous hydrogen iodide in **sulphur dichloride,** S_2Cl_2, forms iodine, sulphur, and hydrogen sulphide. A. J. Bessou finds that hydrobromic acid reacts with **pyrosulphuryl chloride,** $S_2O_5Cl_2$, forming sulphur di- and tri-oxides, hydrogen chloride, bromine, and chlorosulphonic acid, $HO.ClSO_2$, and finally sulphuric acid; with hydriodic acid, some sulphur and hydrogen sulphide are formed.

According to A. J. Balard,[11] conc. **sulphuric acid** is reduced by hydrobromic acid, forming sulphur dioxide, water, and bromine. The reaction is symbolized: $2HBr+H_2SO_4=2H_2O+SO_2+Br_2$; there is a partial removal of the gaseous substances from the system. In dil. soln. the products all remain in soln. and a state of equilibrium is attained: $2HBr+H_2SO_4 \rightleftharpoons SO_2+2H_2O+Br_2$. J. L. Gay Lussac observed a similar reaction with hydriodic and sulphuric acids: $H_2SO_4+2HI=SO_2+2H_2O+I_2$; and E. Soubeiran noted that if the soln. be diluted, sulphur dioxide and iodine react to form sulphuric and hydriodic acids. F. T. Addyman found that with potassium bromide, KBr, and sulphuric acid, H_2SO_4,

Ratio of acid to salt . . .	2 : 2	3 : 2	4 : 2	5 : 2	6 : 2
HBr decomposed	8·31	15·53	19·88	26·91	31·30 per cent.

so that the amount of decomposition is nearly proportional to the amount of sulphuric acid employed. Similarly with hydrobromic acid, as illustrated in Table XVI, which shows that there is very little decomposition with 30 per cent. hydrobromic acid, but in a stronger acid the amount of decomposition becomes more marked. In the table 5 c.c. of hydrobromic acid contained 0·81 grm. HBr.

According to P. T. Austen,[12] there is no reaction when hydrogen chloride is warmed with the vapour of **nitric acid,** HNO_3, although there is a feeble reaction between the vapour of nitric acid and hydrogen bromide, and when the vapour of nitric acid is led into hydrogen iodide a fine red flame appears, and iodine separates. A mixture of hydrochloric and nitric acids forms aqua regia which readily decomposes with the evolution of chlorine, and the formation of nitrogen peroxide, NO_2, nitrosyl chloride, NOCl, or nitroxyl chloride, NO_2Cl, according to circumstances. According to A. J. Balard, a mixture of nitric and hydrochloric acids reacts with hydrobromic acid, slowly forming nitrogen peroxide, water, and bromine. Aqua regia, and the corresponding mixture with hydrobromic in place of hydrochloric acid, both dissolve gold. The slow reaction between hydriodic and nitric acids has been symbolized by A. Eckstädt: $HNO_3+2HI=HNO_2+H_2O+I_2$. The velocity of the reaction is slackened by decreasing the concentration of the reacting substances. When about two-thirds of the hydriodic acid has been decomposed, the velocity is augmented and the reaction quickly runs to an end. This is attributed to the formation of tri-iodide by the union of the iodine with the hydriodic acid, when one-third of the latter acid has been so converted. The free iodine itself then forms hydriodic acid, and the oxidizer restarts the reaction. Ferrous salts act catalytically. Scratches on the flask also accelerate the reaction. Carbamide slows down the reaction, presumably by destroying nitrous acid formed as an intermediate stage in the reaction.

TABLE XVI.—ACTION OF SULPHURIC ACID ON HYDROBROMIC ACID.

98 per cent. sulphuric acid.		Per cent. of HBr decomposed
Volume used.	Per cent. H_2SO_4 in solution.	
0·3	—	—
0·7	20·79	—
1·0	27·27	trace
1·2	31·03	0·04
2·0	42·86	0·06
3·0	52·94	0·16
4·0	60·00	0·54
6·0	69·23	0·53
8·0	75·00	0·64

According to P. T. Austen, **nitrous oxide,** N_2O, forms a white cloud, which gradually reddens and deposits crystals of iodine; *the liquid which collects at the bottom of the flask contains some ammonia*: $N_2O+10HI=2NH_4I+H_2O+4I_2$. According to E. J. Chapman, hydriodic acid slowly absorbs **nitric oxide,** NO, forming ammonia, etc. J. L. Gay Lussac observed the formation of iodine, water, and nitric oxide with a mixture of hydrogen iodide and nitrogen peroxide, or nitrous acid. According to L. W. Winkler, a mixture of potassium iodide and **nitrite,** when treated drop by drop with sulphuric acid of concentration 50 per cent., furnishes highly pure nitric oxide: $2NHO_2+2HI=2NO+I_2+2H_2O$. **Nitrous acid** forms nitric oxide and chlorine together with some hydrochloric acid. The **nitrates** are attacked and converted into chlorides by hydrogen chloride. According to R. E. Hughes, if dry hydrogen chloride be passed over dry silver nitrate at ordinary temp., or at 100°, only about one per cent. of the theoretical change occurs; and the dry gas produces but a slight turbidity in a soln. of silver nitrate in hot dry benzene or ether. The hydrogen halides unite with **ammonia,** forming the corresponding ammonium halide: *e.g.* $NH_3+HCl=NH_4Cl$, but there is no reaction, say R. E. Hughes and H. B. Baker,[13] if the hydrogen chloride and ammonia be thoroughly dried. According to J. Ogier,[14] hydrogen chloride unites with **phosphine,** PH_3, forming phosphonium chloride, PH_4Cl, at $-35°$ under atm. press.; and at 14° under a press. of 20 atm. When

conc. hydrochloric acid is heated with amorphous **phosphorus** for some hours at about 200°, A. Oppenheim found that some phosphine, PH_3, is formed. A. Damoiseau found that while hydrobromic acid does not act on phosphorus in the cold, in sealed tubes, at 100°–120°, considerable quantities of phosphonium bromide are formed, but not phosphorus bromide, since phosphorus tribromide is slowly decomposed by a conc. soln. of hydrobromic acid. A. Richardson found that moist red phosphorus and hydrogen bromide react in sunlight. If a current of hydrogen iodide be led over yellow phosphorus at ordinary temp., phosphonium iodide, PH_4I, and some phosphorus di-iodide, PI_2, are formed : $5P+8HI=2PH_4I+3PI_2$. With red phosphorus there is no reaction, even at 100°. Hydriodic acid acts in a similar manner, but less rapidly, provided the hydriodic acid is in excess : if the phosphorus be in excess, the reaction is modified by the water since water decomposes phosphorus di-iodide ; the final products are phosphonium iodide and phosphorous acid : $2P+HI+3H_2O=PH_4I+H_3PO_3$. **Phosphorus pentoxide,** P_2O_5, say G. H. Bailey and G. T. Fowler, absorbs about 227 c.c. of hydrogen chloride gas per gram. The rate of absorption commences very slowly, rises to a maximum in about 120 hours, and then gradually diminishes, finally ceasing altogether in over 600 hours. It is believed that there is a slow reaction resulting in the formation of phosphoryl chloride, $POCl_3$, and metaphosphoric acid : $2P_2O_5+3HCl=POCl_3+3HPO_3$. H. Moissan observed that the reaction between hydrogen fluoride and phosphorus pentoxide is due to the formation of phosphoryl fluoride, POF_3. Phosphorus pentoxide also absorbs hydrogen bromide, but not hydrogen iodide ; in the former case, phosphoryl bromide, $POBr_3$, is slowly formed, even more slowly than in the case of phosphoryl chloride.

Hydrogen chloride acts on but few of the metalloids at ordinary temp., or even when heated. It inflames in contact with **fluorine;** it forms chlorine when heated with **oxygen ;** and it forms a mixture of silicon tetrachloride, $SiCl_4$, and silicochloroform, $SiHCl_3$, when heated to redness with amorphous **silicon.** Most of the **metals,** when heated with hydrogen chloride, form chlorides with the evolution of hydrogen. According to M. Ribalkin, the reaction with **silver**[15] commences at about 117° and progresses with an increasing velocity up to 200°. The reaction is reversible in that silver chloride is reduced by hydrogen : $2AgCl+H_2\rightleftharpoons 2Ag+2HCl$. **Magnesium, sodium,** or **potassium** burn momentarily in hydrogen iodide and the flame then expires. A. Potilitzin found 96·5 per cent. of hydrogen iodide reacted with silver in 6 days. M. Ribalkin also noted that with **copper** for equilibrium, 93 per cent. of hydrogen chloride is decomposed at 230°, and 66 per cent. at 440° ; with cuprous chloride and hydrogen : $2CuCl+H_2=2Cu+2HCl$, there is no reaction at 200° ; at 230°, 5 per cent. of hydrogen chloride is formed and 35 per cent. at 440°. According to A. Richardson, dry hydrogen iodide is completely decomposed by contact with dry copper. The action of hydrogen chloride on warm **aluminium** (160°), copper, or silver was found to be accompanied by an emission of electrons as evidenced by electrical conductivity. **Mercury** is not attacked by hydrogen chloride, but G. H. Bailey and G. J. Fowler found a white skin of mercurous oxychloride, Hg_2OCl_2, is formed on the surface of mercury confining a mixture of hydrogen chloride and oxygen—in darkness or in light. Similar remarks apply to mixtures of oxygen with hydrogen bromide or iodide. Hydrogen bromide or iodide alone, dry, and free from oxygen, are almost completely decomposed in light or in darkness when in contact with mercury. M. Berthelot found that a quantity of hydrogen bromide which decomposed in 50 hrs. at 100°, when in contact with mercury, required a year to decompose it at ordinary temp. Hydrochloric acid dissolves the metals of the alkalies and alkaline earths, **zinc,** magnesium, **cadmium,** aluminium, **manganese, nickel, cobalt, iron,** and **chromium** with the formation of the chlorides and the evolution of hydrogen ; and it dissolves the metals of the fifth and sixth groups. **Lead** is slowly, and **tin** and copper very slowly, attacked in a similar manner. Silver, mercury, **arsenic, antimony, bismuth, gold,** and **platinum** are not dissolved. Hydrobromic and hydriodic acids also dissolve many of the metals, forming bromides or iodides respectively with the

liberation of hydrogen. According to A. Ditte and R. Metzner,[10] antimony dissolves in hydrochloric acid in the presence of oxygen. Platinum black or platinum sponge is slowly attacked by hydrochloric acid in the presence of air—say occluded oxygen—forming hydrochloroplatinic acid, H_2PtCl_6: platinum foil, gold, and **tellurium** are likewise attacked under similar conditions if heated some hours at 170°. According to C. Matignon, these reactions occur at a much lower temp. than that at which hydrogen chloride is appreciably affected by oxygen. M. Berthelot found that fuming hydrochloric acid attacks gold and platinum in light, and particularly if some manganese chloride is present. Seleniferous hydrochloric acid, says J. E. Gerock, dissolves copper much more rapidly than if selenium be absent. The rate of soln. of magnesium in hydrochloric, hydrobromic, and hydriodic acids is discussed by N. Kajander; and the rate of soln. of plumbiferous zinc by W. Spring and E. van Aubel; and of chromium by T. Döring. According to W. Hittorf, passive chromium is activated by hydrochloric, hydrobromic, or hydriodic acid.

Hydrochloric acid decomposes the insoluble **oxalates, carbonates, hypophosphites, phosphates, hydrides,** and **sulphites.** Ferrous, manganese, and zinc **sulphides** are readily dissolved by hydrochloric acid; silver, cadmium, copper, lead, tin, cobalt, nickel, antimony, and bismuth sulphides are dissolved by the conc. acid; arsenic tri- and penta-sulphides are dissolved only by the hot conc. acid; red mercuric sulphide is insoluble, while the black sulphide is slowly dissolved by the hot conc. acid. Most of the metal **oxides** and **hydroxides** are converted into chlorides by treatment with hydrochloric acid—*e.g.* lead, tin, arsenic, antimony, bismuth, copper, silver, gold, molybdenum, chromium, aluminium, cobalt, nickel, iron, manganese, cadmium, zinc, and the oxides of the alkalies and alkaline earths. Similar remarks apply to hydrobromic and hydriodic acids. The ignited oxides react more slowly than when freshly precipitated or dried at 100°, and the calcined oxides of chromium, iron, aluminium, etc., require a very prolonged boiling with the hydrochloric acid to effect soln. W. Spring[17] has studied the rate of dissolution of marble or Iceland spar in the haloid acids. E. F. Smith and F. L. Meyer found that the hydrogen halides expel all the nitrogen from **nitrates**; phosphates are but slightly affected; arsenic is partially volatilized from **arseniates** by hydrogen fluoride, and completely removed by the other halides; hydrogen chloride expels all the antimony from **antimoniates**; and hydrogen fluoride or bromide volatilizes part of the vanadium from **vanadates,** and hydrogen chloride drives off all that metal. The metal **dioxides**—*e.g.* manganese dioxide, lead dioxide, chromic anhydride, etc.—with hydrochloric acid form the corresponding chloride, and chlorine. Hydrogen chloride acts on dry manganese dioxide whether moisture is excluded or not. There is a vigorous reaction between **chromic anhydride,** CrO_3, and hydrogen chloride, much heat is developed, and chromyl chloride, CrO_2Cl_2, is formed: a similar reaction occurs with 35 to 40 per cent. hydrochloric acid, but the yield of chromyl chloride is reduced the more dil. the acid, until, with 20 per cent. hydrochloric acid, chlorine alone is formed.[18] The **permanganates, persulphates, chromates,**[19] etc., furnish chlorine, etc. **Caro's acid** liberates chlorine from hydrochloric acid, but with hydrofluoric acid, neither fluorine nor ozone is produced—the latter, if formed, would have been taken as evidence of the transient appearance of fluorine. **Ferric salts** are reduced to ferrous salts by hydriodic acid. Some of the **carbides, borides,** and metal **silicides** are readily attacked by hydrochloric, hydrobromic, or hydriodic acid. The reaction between hydriodic acid and the chromates has been studied by W. Ostwald;[20] between hydriodic acid and the persulphates by T. S. Price.[21]

Hydrochloric acid is one of the strongest of acids, but if moisture be excluded, G. Wilson noticed, in 1859, that hydrogen chloride gas does not even redden blue litmus. R. E. Hughes and F. R. L. Wilson[22] found no appreciable increase in weight on treating dry Iceland spar at 130° for an hour with dry hydrogen chloride; with the moist gas, there was approximately 3 per cent. increase in weight. This confirms an observation made by W. Higgins in 1814: "Dry muriatic acid has no action on dry calcareous earth, while these substances readily unite if moisture be

conc. hydrochloric acid is heated with amorphous **phosphorus** for some hours at about 200°, A. Oppenheim found that some phosphine, PH_3, is formed. A. Damoiseau found that while hydrobromic acid does not act on phosphorus in the cold, in sealed tubes, at 100°–120°, considerable quantities of phosphonium bromide are formed, but not phosphorus bromide, since phosphorus tribromide is slowly decomposed by a conc. soln. of hydrobromic acid. A. Richardson found that moist red phosphorus and hydrogen bromide react in sunlight. If a current of hydrogen iodide be led over yellow phosphorus at ordinary temp., phosphonium iodide, PH_4I, and some phosphorus di-iodide, PI_2, are formed: $5P+8HI=2PH_4I+3PI_2$. With red phosphorus there is no reaction, even at 100°. Hydriodic acid acts in a similar manner, but less rapidly, provided the hydriodic acid is in excess; if the phosphorus be in excess, *the reaction is modified by the water since water decomposes phosphorus di-iodide*; the final products are phosphonium iodide and phosphorous acid: $2P+HI+3H_2O=PH_4I+H_3PO_3$. **Phosphorus pentoxide,** P_2O_5, say G. H. Bailey and G. T. Fowler, absorbs about 227 c.c. of hydrogen chloride gas per gram. The rate of absorption commences very slowly, rises to a maximum in about 120 hours, and then gradually diminishes, finally ceasing altogether in over 600 hours. It is believed that there is a slow reaction resulting in the formation of phosphoryl chloride, $POCl_3$, and metaphosphoric acid: $2P_2O_5+3HCl=POCl_3+3HPO_3$. H. Moissan observed that the reaction between hydrogen fluoride and phosphorus pentoxide is due to the formation of phosphoryl fluoride, POF_3. Phosphorus pentoxide also absorbs hydrogen bromide, but not hydrogen iodide; in the former case, phosphoryl bromide, $POBr_3$, is slowly formed, even more slowly than in the case of phosphoryl chloride.

Hydrogen chloride acts on but few of the metalloids at ordinary temp., or even when heated. It inflames in contact with **fluorine;** it forms chlorine when heated with **oxygen**; *and it forms a mixture of silicon tetrachloride,* $SiCl_4$, *and silico*chloroform, $SiHCl_3$, when heated to redness with amorphous **silicon.** Most of the **metals,** when heated with hydrogen chloride, form chlorides with the evolution of hydrogen. According to M. Ribalkin, the reaction with **silver**[15] commences at about 117° and progresses with an increasing velocity up to 200°. The reaction is reversible in that silver chloride is reduced by hydrogen: $2AgCl+H_2\rightleftharpoons 2Ag+2HCl$. **Magnesium, sodium,** or **potassium** burn momentarily in hydrogen iodide and the flame then expires. A. Potilitzin found 96·5 per cent. of hydrogen iodide reacted with silver in 6 days. M. Ribalkin also noted that with **copper** for equilibrium, 93 per cent. of hydrogen chloride is decomposed at 230°, and 66 per cent. at 440°; with cuprous chloride and hydrogen: $2CuCl+H_2\rightleftharpoons 2Cu+2HCl$, there is no reaction at 200°; at 230°, 5 per cent. of hydrogen chloride is formed and 35 per cent. at 440°. According to A. Richardson, dry hydrogen iodide is completely decomposed by contact with dry copper. The action of hydrogen chloride on warm **aluminium** (160°), copper, or silver was found to be accompanied by an emission of electrons as evidenced by electrical conductivity. **Mercury** is not attacked by hydrogen chloride, but G. H. Bailey and G. J. Fowler found a white skin of mercurous oxychloride, Hg_2OCl_2, is formed on the surface of mercury confining a mixture of hydrogen chloride and oxygen—in darkness or in light. Similar remarks apply to mixtures of oxygen with hydrogen bromide or iodide. Hydrogen bromide or iodide alone, dry, and free from oxygen, are almost completely decomposed in light or in darkness when in contact with mercury. M. Berthelot found that a quantity of hydrogen bromide which decomposed in 50 hrs. at 100°, when in contact with mercury, required a year to decompose it at ordinary temp. Hydrochloric acid dissolves the metals of the alkalies and alkaline earths, **zinc,** magnesium, **cadmium,** aluminium, **manganese, nickel, cobalt, iron,** and **chromium** with the formation of the chlorides and the evolution of hydrogen; and it dissolves the metals of the fifth and sixth groups. **Lead** is slowly, and **tin** and copper very slowly, attacked in a similar manner. Silver, mercury, **arsenic, antimony, bismuth, gold,** and **platinum** are not dissolved. Hydrobromic and hydriodic acids also dissolve many of the metals, forming bromides or iodides respectively with the

liberation of hydrogen. According to A. Ditte and R. Metzner,[16] antimony dissolves in hydrochloric acid in the presence of oxygen. Platinum black or platinum sponge is slowly attacked by hydrochloric acid in the presence of air—say occluded oxygen—forming hydrochloroplatinic acid, H_2PtCl_6 : platinum foil, gold, and **tellurium** are likewise attacked under similar conditions if heated some hours at 170°. According to C. Matignon, these reactions occur at a much lower temp. than that at which hydrogen chloride is appreciably affected by oxygen. M. Berthelot found that fuming hydrochloric acid attacks gold and platinum in light, and particularly if some manganese chloride is present. Seleniferous hydrochloric acid, says J. E. Gerock, dissolves copper much more rapidly than if selenium be absent. The rate of soln. of magnesium in hydrochloric, hydrobromic, and hydriodic acids is discussed by N. Kajander; and the rate of soln. of plumbiferous zinc by W. Spring and E. van Aubel; and of chromium by T. Döring. According to W. Hittorf, passive chromium is activated by hydrochloric, hydrobromic, or hydriodic acid.

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present." The action of hydrogen chloride in non-aqueous solvents has been already discussed.

Liquid hydrogen chloride also exhibits but few acid properties, as has been demonstrated mainly by G. Gore. For example, he found that the liquid possesses but a feeble solvent action, is somewhat inert, and, with the exception of aluminium, exerts but little action on the metals. The liquid does not dissolve the alkali chlorides, ammonium chloride, nickel chloride, etc.; iodine dissolves to form a purple liquid. The carbonates of the alkalies and alkaline earths, and ammonium are so slowly converted into chlorides that the evolution of carbon dioxide is not noticed. The alkali metals are immediately encrusted with a protective film of insoluble chloride; arsenic, antimony, cadmium, silver, and platinum are not attacked; lead, magnesium, and tin are very slowly attacked; iron, copper, and thallium are superficially attacked. Similarly, liquid hydrogen iodide attacks the metals of the alkalies, silver, mercury, copper, tin, iron, and aluminium; while lead, cadmium, zinc, magnesium, thallium, bismuth, antimony, and arsenic are superficially attacked; while boron and silicon are not attacked. The metal oxides are attacked very slowly by liquid hydrogen chloride, if at all; arsenic, antimony, and zinc oxide are dissolved the last slowly; alumina and silica are not changed; titanic oxide is slightly soluble in the liquid. The sulphides are attacked so slowly by liquid hydrogen chloride that no evolution of gas is noticed—sodium and lead sulphides form the chlorides; antimony sulphide dissolves; realgar does not dissolve; iron sulphide is not changed; calcium phosphate is not dissolved; potassium dichromate is not changed; and lead chromate forms a white mass. Sodium and calcium carbonates are not attacked by liquid hydrogen iodide; copper oxide and manganese dioxide are converted into iodides; sulphur forms hydrogen sulphide and iodine; carbon disulphide is inert and immiscible; sulphur dioxide forms water, hydrogen sulphide, and plastic sulphur; ammonia forms ammonium iodide; and water mixes with the liquid iodide in all proportions. Fats are attacked; ether and many organic compounds form additive products.[23]

The composition of the hydrogen halides.—The composition of hydrogen chloride was determined by J. L. Gay Lussac and L. J. Thénard[24] by synthesis from a mixture of equal volumes of hydrogen and chlorine in diffuse light; and by analysis by heating a piece of potassium in one volume of hydrogen chloride gas—potassium chloride was formed, and half a volume of hydrogen remained. A. J. Balard employed the last-named process for the analysis of hydrogen bromide; and J. L. Gay Lussac, for hydrogen iodide. J. L. Gay Lussac also shook up a sealed tube of hydrogen iodide and some mercury whereby mercury iodide and hydrogen were formed. One end of the sealed tube was opened under mercury and the residual hydrogen was found to be equal to half the original volume of hydrogen iodide. The lecture table processes of demonstrating the composition of hydrogen chloride are as follows:

1. *Analysis of hydrogen chloride by sodium amalgam.*—A stoppered glass tube—about 70 cm. long and 1·5 cm. in diameter—is filled with dry hydrogen chloride over mercury. Sodium amalgam is then dropped into the tube, and the tube *immediately* closed with its stopper. The tube is inverted several times in succession, and then opened while its mouth is dipping under mercury. Mercury rushes into the tube, and the residual gas is brought under atm. press. by raising or lowering the tube until the mercury inside and outside is at the same level. The volume of the residual gas is noted. The residual gas can then be tested in the usual manner. It is hydrogen. The hydrogen chloride reacts with the sodium of the mercury amalgam, forming sodium chloride and liberating hydrogen. The object of using sodium amalgam in place of metallic sodium is one of convenience. This experiment demonstrates that **hydrogen chloride contains half its own volume of hydrogen.** Hence, from Avogadro's hypothesis, one molecule of hydrogen chloride contains half a molecule, that is, one atom of hydrogen. The formula is therefore HCl_x, where x represents the number of atoms of chlorine in the molecule. The vapour density of hydrogen chloride is nearly 36·5 ($H_2=2$). Hence the mol. wt. is 36·5, and the weight of hydrogen in the molecule is 1. The molecule of hydrogen chloride thus contains $36·5-1=35·5$ parts of chlorine for every part of hydrogen.

2. *The electrolysis of hydrochloric acid.*—When conc. hydrochloric acid is electrolyzed, a

mixture of equal volumes of hydrogen and chlorine is obtained. Carbon electrodes are used because the chlorine slowly attacks platinum. Chlorine gas is also soluble in conc. hydrochloric acid, so that the acid should be sat. with chlorine before the attempt is made to measure the gaseous products of electrolysis. The vessel containing the acid is arranged so that the acid about one electrode is connected with the acid about the other electrode by a glass tube junction,[32] and an electric current is passed until the liquid in the chlorine limb is sat. with chlorine. The two gas receivers are put into communication with the electrolytic vessel by suitably turning the three-way stopcocks. The gas receivers have, of course, been previously filled with liquid—a sat. soln. of sodium chloride—by placing a dish of the liquid below each receiver and applying suction at the proper exit tube when the three-way cocks are suitably turned. The gases collect in the tubes at equal rates. The experiment shows that **during the electrolysis of concentrated hydrochloric acid, the volume of hydrogen liberated at the one electrode is equal to the volume of chlorine liberated at the other electrode.** Assuming that the hydrogen chloride dissolved in the water is alone decomposed by the electric current, it follows that hydrogen chloride contains equal volumes of hydrogen and of chlorine, and therefore also an equal number of atoms; or the formula is H_xCl_x, where x is evaluated as before from the vapour density 36·5. This demonstration of the composition of hydrogen chloride, though interesting as circumstantial evidence, is not a *proof* unless supported by accessory evidence. A similar demonstration applied to the analogous hydrofluoric acid would "prove" that hydrogen fluoride is a compound of hydrogen and oxygen.

3. *The synthesis of hydrogen chloride.*—The mixed gases obtained by the electrolysis of conc. hydrochloric acid are passed through a stout glass explosion tube with a stopcock at each end. The tower is packed with lime and glass wool to absorb the chlorine. Instead of the tower, the exit tube may lead to the fume closet. When all the air is displaced, the stopcocks are closed. One of the stopcocks may be opened while the corresponding end of the tube is dipping under conc. sulphuric acid; no gas enters or leaves the apparatus. The tube and contents are exposed to sunlight or to the light from burning magnesium. The face must be protected in case the tube should burst during the explosion. When the tube is cold, open one of the stopcocks while the corresponding end is dipping under conc. sulphuric acid; no gas enters or leaves the tube. This shows that no change in volume has taken place as a result of the explosion. It can be proved that the tube contains nothing but hydrogen chloride by opening the tip of the tube under water. The hydrogen chloride will be absorbed and water will rise and fill the tube except for a little air (or perhaps a slight excess of hydrogen) which might have been present. This experiment shows that **one volume of hydrogen unites with one volume of chlorine to form two volumes of hydrogen chloride.**

Hydrogen chloride contains the eq. of half its volume of chlorine and half its volume of hydrogen, or, by Avogadro's hypothesis, assuming the hydrogen and chlorine each contain two atoms, one molecule of hydrogen chloride contains half a molecule of chlorine, that is, one molecule of hydrogen chloride contains an atom of chlorine and an atom of hydrogen. The formula is therefore HCl. This agrees with the vapour density determination of hydrogen chloride which furnishes 36·49 (H_2=2). If the at. wt. of chlorine be 35·46, and of hydrogen 1·008 (O=16), it follows that the formula for hydrogen chloride is HCl.

The detection and determination of the chlorides, bromides, and iodides.—A soln. of **silver nitrate** produces a very sparingly soluble precipitate of silver chloride, bromide, or iodide when added to a neutral or acid soln. of the corresponding acid or salt. Silver chloride and bromide are white, silver iodide is pale yellow. The precipitates are all virtually insoluble in dil. nitric acid, and in a soln. of potassium cyanide or sodium thiosulphate. Silver chloride is easily soluble in aq. ammonia, silver bromide is less soluble, and the iodide is but sparingly soluble. Ammonium carbonate (sesqui- or bicarbonate) dissolves silver chloride fairly easily, but not the bromide or iodide. Silver nitrate does not precipitate all the chlorine from soln. of mercuric chloride unless a large excess of the nitrate is used. Stannous chloride also reduces some of the silver to the metallic state; the precipitate with platinic chloride is yellow owing to the presence of some platinum. Green chromic chloride also gives no precipitate with silver nitrate. **Mercurous nitrate** gives a white precipitate of mercurous chloride, a pale yellow precipitate of mercurous bromide, and a yellowish-green precipitate of mercurous iodide respectively with neutral or acid soln. of chlorides, bromides, or iodides. Soln. of **lead acetate** or **lead nitrate** give crystalline precipitates in cold conc. soln. of the halides—the chloride

and bromide are white and the iodide is yellow. The precipitates are fairly soluble in hot water. **Thallous sulphate,** Tl_2SO_4, gives a white precipitate in conc. soln. of the chlorides, or bromides, and a deep yellow precipitate with iodides. **Palladium chloride,** $PdCl_2$, has no action on soln. of chlorides or bromides, but **palladium nitrate,** $Pd(NO_3)_2$, gives a brown precipitate, $PdBr_2$, with bromides, but not with chlorides; both palladium salts give a very dark brown precipitate, PdI_2, with iodides. **Mercuric chloride** in excess gives no precipitate with chlorides or bromides, but with iodides a scarlet precipitate, HgI_2, is obtained. This precipitate is soluble if the potassium iodide be in excess. Iodides alone are decomposed by **ferric sulphate** with the liberation of the free halogen. A mixture of **copper sulphate** and sulphurous acid added in excess to a conc. soln. of a chloride, bromide, or iodide, gives a precipitate of the corresponding cuprous chloride, CuCl, or bromide, CuBr, or iodide, CuI. Stannous chloride can be used instead of sulphurous acid. A soln. of cuprous chloride in an excess of ammonium chloride gives a white precipitate of cuprous iodide, CuI. Dil. **sulphuric acid** (1 : 10) has no action on chlorides cold or hot; it has no action on cold soln. of the bromides or iodides, but gives off hydrogen bromide or iodide respectively when heated. Conc. sulphuric acid partially decomposes solid chlorides in the cold and completely when heated. Hydrogen chloride is evolved. Silver and mercurous chlorides are decomposed with difficulty, the latter gives off some sulphur dioxide as well as hydrogen chloride: $2HgCl+3H_2SO_4=2HgSO_4+2H_2O+SO_2+2HCl$. Bromides under similar conditions give both bromine and hydrogen bromide; and with iodides, iodine is formed and some sulphuric acid is reduced to sulphurous acid: $2NaI+2H_2SO_4=Na_2SO_4+H_2O+H_2SO_3+I_2$; and with an excess of hydriodic acid the sulphuric acid is reduced to hydrogen sulphide: $H_2SO_4+8HI=4H_2O+H_2S+4I_2$. If the chloride, bromide, or iodide is mixed with sulphuric acid and **manganese dioxide,** there is an evolution of chlorine, bromine, or iodine respectively. Free hydrochloric acid can be detected in a soln. of a chloride by distilling the soln. with manganese dioxide alone, and collecting the distillate in a soln. of starch and potassium iodide. A blue coloration indicates that hydrochloric acid was present. Alkali chlorides or bromides are not decomposed if melted with **potassium dichromate**; but the iodides liberate iodine. If a dry decomposable chloride is heated with a mixture of **concentrated sulphuric acid and potassium dichromate,** reddish-brown vapours of chromyl chloride, CrO_2Cl_2, are evolved which condense to a brown liquid. This chloride is decomposed by water forming chromic and hydrochloric acids: $CrO_2Cl_2+2H_2O=H_2CrO_4+2HCl$. If treated with sodium or potassium hydroxide, a mixture of the alkali chloride, etc., is formed. If such a soln. be acidified and shaken with ether and hydrogen peroxide, the upper ethereal layer will be coloured blue, and this coloration indicates chromium, which in turn shows that a chloride was originally present. With bromides, bromine, and with iodides, iodine; but no chromium collects in the distillate. Chlorides, bromides, or iodides when heated with a mixture of dil. sulphuric acid and potassium dichromate give respectively free chlorine, bromine, or iodine. **Chlorine water** with bromides liberates bromine, which can be recognized by the yellow or brown coloration, particularly if shaken with a little chloroform or carbon disulphide in which the bromine dissolves. Iodides behave similarly, but impart a rose or violet colour to the chloroform or carbon disulphide; **bromine water** liberates iodine from iodides alone. **Alkali nitrates** and dil. sulphuric acid have no action on chlorides or bromides, but with iodides, iodine is liberated, and this can be recognized by the blue coloration it imparts to a soln. of starch. In *I. Guareschi's test for bromine* (1912),[26] H. Schiff's reagent for the detection of aldehydes is made by just decolorizing a soln. of magenta S (or rosaniline acetate, *p*-rosaniline hydrochloride, Hofmann's violet, etc.) by means of sulphur dioxide (or sodium bisulphite). A trace of bromine gives an intense violet-blue coloration, iodine gives virtually no coloration, and chlorine a brownish-yellow or red tint. The coloration shows with 0·00001 grm. of potassium bromide in 0·1 c.c. of soln. after treatment with 2 c.c. of 25 per cent. chromic acid. The liquid is shaken with ether and the colour collects between the

ethereal and aq. layers. In testing for bromine vapour, the reagent is best absorbed on blotting paper free from starch, and this suspended over the liquid in which the bromine is liberated by chlorine water, chromic acid, etc. The reaction is hindered by nitrites which must be removed; thiocyanates give no reaction or a faint rose coloration. The colour given with aldehyde and the magenta reagent is reddish-violet, and is not removed from the soln. by ether; the colour is produced only in soln., and not by the vapour of aldehyde.

Most insoluble chlorides are decomposed by boiling with a conc. soln. of **sodium carbonate**: $2HgCl+Na_2CO_3=2NaCl+CO_2+Hg_2O$, and the soln. of alkali chloride is freed by filtration from the heavy metal. Silver chloride is not decomposed by this treatment, but even it is decomposed by fused sodium carbonate. Silver chloride may also be decomposed by treatment with cadmium or zinc in an acid soln. Many chlorides of the non-metals are decomposed by water with the formation of hydrochloric acid: $PCl_5+4H_2O=H_3PO_4+5HCl$; carbon tetrachloride must be heated with water in a sealed tube: $CCl_4+2H_2O=CO_2+4HCl$. Many organic chlorides are decomposed: (i) By heating in a sealed glass tube with silver nitrate and conc. nitric acid—L. Carius' process. (ii) By heating an intimate mixture of the chloride with granular lime and subsequently extracting the mass with dil. nitric acid. (iii) By heating the substance with a small piece of clean sodium, or magnesium wire. The cold mass is extracted with water.

Chlorides, bromides, and iodides can be quantitatively determined by treatment with silver nitrate, and, with suitable precautions, the precipitated halide is washed, dried, and weighed. Chlorides in neutral soln. can be determined by *F. Mohr's volumetric process* [27] by titration with a standard soln. of silver nitrate with a little potassium chromate or sodium phosphate as indicator. When all the chloride has reacted with the silver nitrate, any further addition of this salt gives a yellow coloration with the phosphate, and a red coloration with the chromate. In *J. Volhard's volumetric process*, the chloride is treated with an excess of an acidified soln. of silver nitrate of known concentration. The excess of silver nitrate is filtered from the precipitated chloride, and titrated with a standard soln. of ammonium thiocyanate, NH_4CNS—a little ferric alum is used as indicator. When the silver nitrate is all converted into thiocyanate: $AgNO_3+NH_4CNS=AgCNS+NH_4NO_3$, the blood-red coloration of ferric thiocyanate appears.

A. du Pasquier [28] in 1840 and M. J. Fordos and A. Gélis in 1842 indicated the principle of the process for the volumetric determination of iodine by means of sodium thiosulphate: $2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6$, but the results were not satisfactory. R. Bunsen used a standard soln. of sulphurous acid: $H_2SO_3+I_2+H_2O=H_2SO_4+2HI$, and indicated the precautions needed for accurate results. The introduction of sodium thiosulphate in place of sulphurous acid by C. L. H. Schwarz in 1853 proved of noteworthy benefit in analytical processes. A little starch paste is used as indicator, and when the blue colour of the iodine is discharged, the titration is finished. The process is used not so much for the direct determination of iodine in iodine compounds, but rather in the indirect determination of such substances as will liberate iodine when in contact with potassium iodide either by direct displacement—*e.g.* chlorinated compounds, chlorine, etc.—or by reduction in the presence of hydrochloric acid—*e.g.* lead peroxide, chromic acid, manganese peroxide, arsenic acid, ferric chloride, etc. Bromides can be oxidized and the free bromine passed into a soln. of potassium iodide or into a soln. of arsenious acid of known concentration. Alkaline arsenites are transformed by chlorine, bromine, or iodine into arsenates: $K_3AsO_3+H_2O+Cl_2=KH_2AsO_4+2KCl$, the free halogen can be titrated with a standard soln. of sodium thiosulphate, or the excess of arsenious acid titrated with a standard soln. of potassium permanganate: $2KMnO_4+5H_3AsO_3+4H_2SO_4=3H_2O+2KHSO_4+2MnSO_4+5H_3AsO_4$. The separation of chlorides, bromides, and iodides is effected by removing the iodine with some reagent which does not interfere with the other two halides, and separating the chlorides and bromides by oxidizing reactions which break down the bromides but

not the chlorides For example, F. W. Kuster [29] distilled a mixture of the three halides with a soln. of acetic acid and sodium acetate which expelled the iodine; then with a soln. of acetic and sulphuric acids to expel the bromine; and finally with conc. sulphuric acid to expel the chlorine. The methods usually employed depend on the fractional oxidation of the mixture. Iodides are oxidized most readily, and chlorides least readily. L. F. Kebler used conc. nitric acid, but the result is more under control with dil. acid. There is a tendency to the formation of iodic acid. J. von Liebig recommended oxidation with iodic acid, or potassium iodate and sulphuric acid; S. Benedict and J. F. Snell used a mixture of potassium iodate and acetic acid with better results. Several other oxidizing agents have been recommended—lead, manganese, or barium dioxide; alkali chromates, permanganates, nitrites, hypochlorites, arsenates, or persulphates; ferric salts; etc. The processes require a careful adjustment of the acidity of the soln. and on the interruption of the reaction at the right time, otherwise the chloride might be attacked. S Bugarszky's method (1895) [30] is based on the action of potassium di-iodate in dil. sulphuric acid soln. as symbolized by the equation: $KH(IO_3)_2 + 10KBr + 11H_2SO_4 = 11KHSO_4 + 5Br_2 + I_2 + 6H_2O$. The iodine and bromine can be distilled off in a current of steam, and the remaining chloride with the excess of iodic acid. The soln. with the chloride is diluted, acidified with nitric acid, and the chloride titrated by Volhard's process; the bromine is absorbed in a reducing soln.—containing say phosphorous acid—and boiled until all the iodine is expelled and the bromine determined in the residue by Volhard's titration process. G. Denigès liberated the iodine by treatment with sulphuric acid and ferric sulphate; the bromine by potassium dichromate; and the chlorine was liberated from the residue left after the removal of these two halogens. If a soln. of iodides, bromides, and chlorides be boiled with ferric sulphate, the iodine which distils off can be collected in a soln. of potassium iodide and titrated with sodium thiosulphate. The soln. is cooled to 60° and a slight excess of potassium permanganate is added. The bromine is all liberated, and it may be collected in ammonia. Chlorides alone remain in the residue.

Silver chloride is converted into silver bromide by digestion with a soln. of potassium bromide. Silver iodide is scarcely affected by this treatment. Silver chloride and bromide are converted into silver iodide by digestion with potassium iodide. Hence, F. Field devised an ingenious process for the determination of chlorides, bromides, and iodides when all these are together. The soln. is divided into three equal parts. The halogens in each are precipitated with silver nitrate. The precipitate in one is washed, dried, and weighed. Let w be the weight of the precipitate containing x of silver chloride, y of silver bromide, and z of silver iodide. The precipitate in another portion is washed, digested with potassium bromide, washed, dried and weighed. Let w_2 be the weight of the precipitate containing $187{\cdot}8x/143{\cdot}34$ of silver bromide derived from silver chloride, with y of the original bromide and z of the original iodide. The third precipitate is treated with potassium iodide in a similar manner. The weight w_3 of silver iodide contains $234{\cdot}8x/143{\cdot}34$ of silver iodide derived from the chloride; $234{\cdot}8y/187{\cdot}8$ derived from the bromide, and z of the original iodide. Consequently, $w_1 = x + y + z$; $w_2 = 1{\cdot}310x + y + z$; $w_3 = 1{\cdot}638x + 1{\cdot}250y + z$.

Uses of the halide acids.—The hydrochloric acid formed as a by-product in the manufacture of sodium sulphate from sodium chloride is sufficient to meet commercial requirements, and accordingly the acid is cheap. The largest amount of hydrochloric acid or hydrogen chloride is used in the manufacture of chlorine and chlorine products—hypochlorites, bleaching powder, and chlorates. It is also used in the manufacture of many of the metal chlorides—zinc, tin, etc. This acid is also used for general purposes in laboratories, in analytical and metallurgical work, in the manufacture of colours. Smaller quantities are used medicinally. Hydrobromic acid or the bromides and hydriodic acid or the iodides are used medicinally, in photography, and in analytical chemistry. Hydriodic acid is an important

reducing agent.[31] Hydrochloric acid is stored for transport in large glass balloons or carboys, or in stoneware vessels. It cannot be stored in iron or lead vessels because these metals are attacked by the acid.

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§ 12. The Chlorides, Bromides, and Iodides

Many chlorides can be obtained by double decomposition—*e.g.* by treating silver, lead, or mercurous nitrate with hydrochloric acid or a soln. of a soluble chloride, the metal chloride is precipitated: $AgNO_3+HCl=AgCl+HNO_3$; and by treating mercuric chloride with antimony sulphide, gives insoluble mercuric sulphide, and soluble antimony chloride: $Sb_2S_3+3HgCl_2=2SbCl_3+3HgS$. H. Rose[1] transformed a number of compounds into chlorides by heating them with five to eight times their weight of ammonium chloride—*e.g.* alkali sulphates and nitrates—in some cases the conversion is but partial and incomplete—*e.g.* barium sulphate, alkali phosphates, bromides, and iodides. Bromides are usually converted into chlorides, and iodides into bromides or chlorides by treatment with the corresponding acid or halogen. The reaction, however, is often reversible.[2] A. Potilitzin found 5·48 per cent. of bromine was removed from sodium bromide by heating that salt with chlorine in a sealed tube at 20° for 36 hrs., anhydrous barium bromide was not attacked by chlorine below 100°. Potassium bromide cannot be completely converted into chloride by the action of dry chlorine unless at a very high temp., but in the presence of moisture the conversion is completed at moderate temp. Gaseous hydrogen chloride decomposes bromides at a red-heat. P. Julius showed that in the case of silver, iodine vapour converts the bromide or chloride into silver iodide. The general processes of preparation may be classed as follows:

The action of the halogen on the metal.—Many metals unite directly with the halogens: for example, potassium; powdered arsenic, antimony, or bismuth; tin-foil; reduced copper or nickel unite directly with chlorine at ordinary temp., in many cases the reaction being attended by incandescence. Sodium, tungsten, manganese, zinc, mercury, indium, thallium, tellurium, iron, cobalt, lead, silver, gold, and platinum do so when heated. If the gas and metal be thoroughly dried, there is little or no reaction with many of the metals. Potassium, arsenic, antimony, and tin unite with bromine at ordinary temp. with incandescence; bismuth, iron, and mercury do so without incandescence and in the cold; gold slowly unites with bromine in the cold, platinum not at all. Similarly, when iodine is brought in contact with some metals they unite directly in the cold, others require to be heated. The direct union of the halogen with the metal is employed for preparing some anhydrous chlorides and bromides—*e.g.* I. A. Kablukoff's process for aluminium bromide; F. Ducelliez and A. Raymand's process[3] for manganous bromide or iodide; M. Guichard's process for ferrous, nickel, and uranium iodides.

The action of the halogen on the metal oxides, hydroxides, or carbonates. Many compounds of the metals can also be used in place of the metals themselves. Thus, chlorine attacks silver oxide at ordinary temp., and it reacts with incandescence on the heated oxides of the alkaline earths. Chlorides are also formed by the action of chlorine on heated magnesia; alumina reacts with some difficulty, and silica with still greater difficulty, for at a white heat only traces of the silicon chloride are formed. The oxides of zinc, cadmium, copper, nickel, and lead react readily; ferric oxide and cobalt oxide, Co_3O_4, react with difficulty. Molybdenum trioxide, MoO_3; tungsten trioxide, WO_3; chromic oxide, Cr_2O_3, form oxychlorides; while manganese carbonate, antimony pentoxide, arsenic trioxide, and stannous oxide produce a mixture of the chloride and an oxide or acid at low temp. and almost wholly chloride at a high temp. Bromine vapour likewise, when passed over the red-hot alkali hydroxides or the oxides of the alkaline earths, forms the corresponding bromide. Silver oxide reacts with bromine in the cold. Bromine expels carbon dioxide from the carbonates, but does not decompose heated sulphates of potassium, magnesium, or zinc. Iodine vapour acts in a similar way, for if passed over the oxides of certain metals—*e.g.* potassium, sodium, lead, bismuth, etc.—the metal iodide is formed and oxygen is evolved. When barium sulphide is treated with iodine the resulting barium iodide is decomposed by potassium sulphite and converted into soluble potassium iodide and insoluble barium sulphate. Similarly with bromine and barium sulphide.[4]

J. L. Gay Lussac and L. J. Thénard[5] showed in 1811 that if many of the metallic oxides be intimately mixed with carbon the reaction with chlorine proceeds more readily than with the oxide alone; the metal chloride and carbon monoxide or dioxide are the products of the reaction. M. le Quesneville and F. Wöhler used this process for aluminium chloride, chromic chloride, silicon tetrachloride, etc., and C. Baskerville for thorium tetrachloride.

The action of the hydrogen halide or acid on the metal, oxide, carbonate, etc.—Most metal oxides are decomposed by the hydrogen halide or acid, either at ordinary temp. or at a red heat, with the formation of the metal halide and water. The oxides, carbonates, sulphides, etc., are also decomposed with the formation of the metal halide. Soln. of the chlorides, for example, are formed by the action of aq. hydrochloric acid on certain metals, metal oxides, or carbonates; with some metals, aqua regia is used in place of hydrochloric acid—*e.g.* gold, and the platinum metals. Some sulphates[6] are decomposed by hydrogen chloride—*e.g.* the sulphates of cobalt, nickel, copper, sodium, etc. In the older processes of F. Klein (1863)[7] the liquid obtained by the action of bromine on phosphorus and water was neutralized by the addition of lime or magnesia. J. von Liebig used baryta—barium phosphate was precipitated, and the barium bromide was treated with potassium sulphate. The soln. of potassium bromide was filtered or decanted from the precipitated barium sulphate. E. D. Faust mixed sulphur with twelve times its weight of bromine

and milk of lime containing seven of lime. The reaction is symbolized: $S+3Br_2+4CaO=3CaBr_2+CaSO_4$. According to C. Matignon, the metals of the platinum family are transformed into chlorides by the joint action of conc. hydrochloric acid and air, for example, platinum black in contact with hydrochloric acid slowly forms hydrochloroplatinic acid, H_2PtCl_6, at ordinary temp. when air is passed through the liquid, platinum foil also dissolves slowly at 170° under similar conditions, gold foil acts in a similar manner, but the amorphous gold powder which has no metallic lustre is not attacked. Palladium foil dissolves slowly in hydrochloric acid in a globe filled with oxygen; ruthenium sponge is slowly attacked at ordinary temp., more rapidly at 125°; iridium free from iron is not attacked at ordinary temp., but is appreciably attacked at 150°; granular rhodium does not react in the cold, it is slowly attacked at 150°, rapidly at 200°; and osmium dissolves slowly at 150°. A rod of tellurium partially immersed in hydrochloric acid forms small pale yellow drops of tellurium chloride, $TeCl_4$, near the surface of the acid in the neighbourhood of the rod. The action of hydrochloric acid and oxygen on sublimed tellurium is slow at ordinary temp., rapid at 100°.

The action of a mixture of sulphur monochloride and chlorine on the oxides.—The action of a mixture of sulphur monochloride, S_2Cl_2, and chlorine on oxides or oxysalts furnishes anhydrous chlorides—if the chloride is readily volatile, the chlorine is kept in excess, if it volatilizes with difficulty, the sulphur chloride is kept in excess. In this way C. Matignon and F. Bourion[8] prepared silicon tetrachloride from silicon dioxide at a dark-red heat; thorium tetrachloride from thoria; the double chloride, $2AlCl_3.SCl_4$, from alumina. Tungstic oxide gives the oxychloride, WO_2Cl_2, at a high temp. and $WOCl_4$ at a lower temp. Ferric or chromic oxide at a red heat passes rapidly and completely into the chloride; nickel or cobalt oxide at 400° acts similarly. The oxides of zinc, manganese, and tin are also readily converted into chlorides if the fusion of the mass be avoided. Calcium or barium sulphate, or barium carbonate, also readily form chlorides. The easily reduced oxides are attacked by hydrogen bromide, while other metal oxides are obtained by the joint action of the vapour of sulphur chloride and hydrogen bromide upon the oxide. The sulphur chloride should be vaporized between 60° and 90° to get the bromides free from chlorides: thoria at 135° gives thorium tetrabromide, $ThBr_4$, and at 125° thorium oxybromide, $ThOBr_2$; chromium sesquioxide gives chromium bromide, $CrBr_3$, in black crystalline scales; nickel oxide, salmon-yellow crystals of nickel bromide, $NiBr_2$; cobalt oxide, green crystals of cobalt bromide, $CoBr_2$; ceria, cerium bromide, $CeBr_3$; and other rare earths give similar bromides. All these bromides change the colour of litmus to a wine-red colour and have no action on methyl orange.

The action of carbon tetrachloride or a mixture of chlorine with a hydrocarbon or carbon monoxide on the oxide.—H. N. Warren[9] obtained aluminium chloride by heating the oxide to redness with a mixture of petroleum vapour and hydrogen chloride or chlorine, naphthalene chloride or carbon tetrachloride was also used. The bromide was prepared in a similar manner. E. Demarçay used the vapour of carbon tetrachloride, the chlorides of chromium, titanium, niobium, tantalum, zirconium, cobalt, nickel, tungsten, and molybdenum; H. Quantin, a mixture of carbon monoxide and chlorine; and W. Heap and E. Newbery, carbonyl chloride.

The reduction of the oxy-salts.—The chlorates, bromates, iodates, and the oxysalts generally lose their oxygen, and are converted into the corresponding chlorides, bromides, or iodides by heat or by certain reducing agents. A. Müntz[10] found the anaerobic bacteria of soils effected the reduction.

When an element forms two or more chlorides, the highest chloride can often be formed by heating a lower chloride in an excess of chlorine—*e.g.* $SnCl_2+Cl_2=SnCl_4$. If the higher chloride be heated, the lower chloride may be formed—*e.g.* $TlCl_3=TlCl+Cl_2$. The lower chloride may form a higher chloride when heated—*e.g.* $3BiCl_2=2BiCl_3+Bi$. Some of the lower chlorides may be formed by the action of hydrogen on the higher chloride at a red heat—*e.g.* titanium, chromium, molybdenum, tungsten, etc. The higher chloride may often be transformed to the lower

chloride by a reducing agent—*e.g.* hydrogen sulphide, zinc, and hydrochloric acid, sulphur dioxide or a sulphite, stannous chloride, titanous chloride, etc., reduce ferric chloride, $FeCl_3$, to ferrous chloride, $FeCl_2$. In some cases the chloride is reduced to metal—*e.g.* gold chloride with ferrous sulphate: $AuCl_3+3FeSO_4=Au+FeCl_3+Fe_2(SO_4)_3$.

Properties of the halides.—The chlorides are usually colourless, some of the bromides are coloured, and still more iodides. Silver chloride and bromide are white, and the iodide is pale yellow; mercuric chloride is white, the iodide is bright scarlet or lemon yellow; mercurous chloride is white, the iodide is green; lead chloride is white, the iodide deep yellow; anhydrous cobalt bromide is green, the hydrated salt, $CoBr_2.6H_2O$, forms red prismatic crystals. The chlorides are usually soluble in water, but silver, mercurous, cuprous, lead, thallous, gold, and platinous chlorides are very sparingly soluble; similar remarks apply to bismuth, antimony, and mercuric oxychlorides. With the exception of silver chloride all these salts are soluble in aqua regia, and excepting silver, aurous, and platinous chlorides, all are soluble in conc. hydrochloric acid. The chlorides of potassium, sodium, and barium are very sparingly soluble in conc. hydrochloric acid. With the exception of mercuric, stannic, and stannous chlorides all chlorides are very sparingly soluble in ether; the deliquescent chlorides of lithium, calcium, and strontium are soluble in absolute alcohol and in amyl alcohol. The bromides are often less soluble than the iodides, and the iodides less soluble than the bromides. The chlorides are usually more volatile than the corresponding metals, and some are volatile liquids—*e.g.* $AsCl_3$, $SbCl_3$, $SnCl_4$—others are readily fusible solids which volatilize at higher temp.—*e.g.* $MgCl_2$, $ZnCl_2$, $AlCl_3$, etc. The bromides are usually less fusible and less volatile than the corresponding chlorides; and the bromides in turn are more fusible and more volatile than the corresponding iodides. Anhydrous lithium and cuprous bromides evolve bromine when heated to their m.p.; sodium, cæsium, and thallium bromides do not. Ammonium and mercurous bromides sublime without giving free bromine. Many of the bromides give off a little bromine when heated with iodine. The halides of the noble metals decompose into the metal and free halogen when heated; cupric chloride is reduced to cuprous chloride; the halides of silver and mercury are not decomposed by fusion in an atm. of *oxygen*; the alkali chlorides and iodides are partially decomposed, and other chlorides or iodides may be completely decomposed by this treatment. The chlorides and iodides may be wholly or partially decomposed by heating them in a stream of *hydrogen*—*e.g.* silver chloride is reduced to the metal; ferric chloride is reduced to ferrous chloride; cadmium chloride is but slowly reduced at a red heat. Many of even the more stable chlorides decompose when heated for a few hours in a current of water vapour—oxides or basic chlorides are formed. The chlorides of the alkalies and alkali earths are partially decomposed by this treatment. Aluminium, stannic, silicon, and other chlorides are more or less hydrolyzed by treatment with water. Similar remarks apply to the bromides and iodides. The evaporation of aq. soln. of the salts which are hydrolyzed by water furnish the hydroxide mixed with the halide as dry residue. The non-volatile chlorides which are not decomposed by heating in air are not generally decomposed when mixed with carbon and heated to a high temp., although if water vapour be present, reduction may take place. J. L. Gay Lussac and L. J. Thénard obtained similar results by heating mixtures of these chlorides with silica, alumina, beryllia, boric oxide, and calcium phosphate. When the chloride is heated with sulphur there is usually little or no action, in some cases sulphur chloride is formed; and with phosphorus the chlorides are decomposed. Phosphorus pentoxide forms phosphoryl chloride when heated with sodium chloride.

The alkali chlorides absorb sulphur trioxide vapour. Sodium chloride forms a chloropyrosulphate, NaS_2O_6Cl. When sulphur trioxide and sodium chloride are gently heated the reaction is symbolized: $2NaCl+4SO_3=Na_2S_2O_7+S_2O_5Cl_2$; at a red heat, sulphur dioxide and chlorine [11] are formed: $2NaCl+2SO_3=Na_2SO_4+Cl_2+SO_2$. According to A. Vogel, the chlorides of the lighter metals—manganese,

zinc, cobalt, iron—are decomposed by conc. sulphuric acid at ordinary temp.; for a complete transformation the chlorides of copper, antimony, and bismuth, require heating with the acid; and the chlorides of arsenic, tin, and mercury(ic) are not completely decomposed at any temp. When conc. sulphuric acid is heated with chromic anhydride or its salts, chromyl chloride distils over; with the dil. acid, chlorine is evolved. Most metal chlorides give chlorine when heated with manganese or lead dioxide and sulphuric acid. Nitric acid converts most of the chlorides more or less completely into nitrates; similar remarks apply to boric, arsenic, and phosphoric acids. The insoluble chlorides are decomposed by fusion with alkali hydroxides, peroxides, or carbonates.

Thermochemistry of the halides.—The heats of formation of the anhydrous fluorides, chlorides, bromides, and iodides are indicated in Table XVII along with the heats of formation in dil. soln. If the heats of combination of the different

TABLE XVII.—THE MOLECULAR HEATS OF FORMATION OF THE HALIDES (CALS. PER GRAM-MOLECULE).

X = F, Cl, Br, or I.	Fluorides.		Chlorides.		Bromides.		Iodides.	
	Formation.	Solution.	Formation.	Solution.	Formation.	Solution.	Formation	Solution.
H, X	38·5	50·3	22·0	39·4	13·5	—	−0·8	—
K, X	110·0	113·6	105·7	101·2	—	—	—	—
Na, X	109·72	109·12	97·9	96·6	90·7	—	74·2	—
Li, X	—	116·88	93·9	102·3	—	—	—	—
NH_4, X	101·25	99·75	76·8	72·8	—	—	—	—
Ba, X_2	224·0	221·5	197·1	198·3	—	—	—	—
Sr, X_2	224·02	—	184·7	195·85	—	—	—	—
Ca, X_2	216·45	—	169·9	187·4	151·6	—	118·6	—
Be, X_2	—	—	155·0	198·3	—	—	—	—
Mg, X_2	209·5	—	151·2	187·1	—	—	—	—
Zn, X_2	—	138·2	97·4	113·0	78·2	93·2	49·2	60·6
Si, X_4	275·9	gas	—	—	—	—	—	—
Cd, X_2	—	121·7	93·7	94·6	76·2	77·2	45·0	44·0
Hg, X	—	—	31·32	—	24·5	—	—	—
Hg, X_2	—	—	62·8	—	60·8	—	44·8	—
Cu, X	—	—	35·4	—	26·0	—	—	—
Cu, X_2	—	88·1	51·4	62·5	34·8	53·0	16·5	—
Au, X	—	—	5·8	—	—	—	−55·0	—
Au, X_3	—	—	22·8	27·2	12·1	8·4	—	—
Ag, X	22·1	25·5	29·2	—	27·7	—	19·7	—
Tl, X	—	54·4	48·6	38·4	—	—	—	—
Pb, X_2	—	—	83·9	77·9	69·0	59·0	42·0	—
Pd, X_2	—	—	40·5	—	—	—	—	—
Fe, X_2	—	125·2	82·2	101·1	70·0	—	38·0	—
Fe, X_3	—	164·9	96·15	127·85	—	—	—	—
Co, X_2	—	120·3	76·7	95·0	—	—	—	—
Ni, X_2	—	119·0	74·7	93·9	—	—	—	—
Sn, X_2	—	—	80·9	—	63·0	—	—	—
Sn, X_4	—	—	129·8	liquid	98·4	liquid	—	—
Mn, X_2	—	153·3	112·0	128·0	100·0	—	68·0	—
Al, X_3	—	275·2	161·8	238·1	120·6	207·5	86·4	—
S, X_2	—	—	128·8	gas	—	—	—	—
As, X_3	—	—	71·5	—	59·1	—	28·8	—
Sb, X_3	—	136·7	91·4	—	64·9	—	29·2	—
Sb, X_5	—	—	104·5	—	—	—	—	—
Bi, X_3	—	—	90·8	—	—	—	—	—
B, X_3	—	219·3	89·1	gas	—	—	—	—
Pt, X_4	—	—	60·2	79·8	42·4	52·2	—	—

elements with chlorine be plotted with the at. wt. of the elements, a periodic curve is obtained as indicated in Fig. 17, where the hyphens denote the want of data.

The heats of formation of the chlorides are uniformly higher than the corresponding bromides, and the heats of formation of the bromides, in turn, are higher than the iodides. As a result, fact and hypothesis show that bromine will displace iodine and chlorine will displace both bromine and iodine *e.g.* $2AgI + Cl_2 = 2AgCl + I_2 + 19·0$ Cals. On the contrary, hydrogen iodide will attack silver chloride forming iodine and hydrogen chloride. The reverse action, $AgCl + HI = AgI + HCl + 13·3$ Cals., corresponds with the fact that the difference between the heats of formation of HCl (22·0) and HI (−0·8) is greater than the difference between the heats of formation of AgCl (29·2) and AgI (19·7). Hence, heat is evolved by the reaction. G. N. Lewis and M. Randall [12] give for the free energy of formation of a Br′-ion, −24,594 cals., and for an I′-ion, −12,304 cals. at 25°.

Chlorine displaces oxygen from most of the oxides if assisted by heat. With the alkalies and alkaline earths, hypochlorites and related bodies are formed. These, however, are decomposed at higher temp. Aluminium chloride is partly decomposed by oxygen at a red heat; the reverse action obtains if the energy of the reaction be strengthened by allowing carbon to act simultaneously with the chlorine, so that instead of an endothermal reaction: $Al_2O_3 + 3Cl_2 = 2AlCl_3 + 3O - 11·7$ Cals., an exothermal reaction: $Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO + 67·2$ Cals. Similarly, bromine displaces oxygen in very many cases, but red-hot aluminium bromide burns in oxygen gas: $4AlBr_3 + 3O_2 = 2Al_2O_3 + 6Br_2$. Manganous chloride is decomposed by oxygen gas contrary to what might be expected from the numbers in the above table, but in this case, not MnO (47·0) but a higher oxide, with a heat of formation of nearly 58 Cals., is produced.

J. L. Gay Lussac has shown that iodine will displace oxygen from sodium and potassium oxides at a dull red heat as would be anticipated from the above data. The reaction is, however, complicated by the formation of basic iodates with the evolution of heat. These disturbing side-reactions explain the difficulty in preparing iodides quite free from iodates. The iodides of calcium, zinc, and iron are decomposed by oxygen; manganous iodide burns in oxygen, and the vapour of aluminium iodide, mixed with oxygen, is explosive. Mercuric and silver iodides are not attacked by oxygen, while the oxides are readily decomposed by a stream of iodine vapour. Lead oxide is decomposed in a stream of iodine vapour, and lead iodide is decomposed by a stream of hot oxygen. In all these cases, the thermochemical data fit in well with the observed facts.

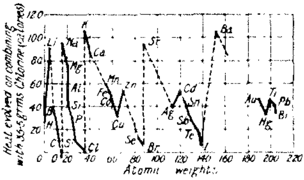

FIG. 17.—Heats of Formation of the Chlorides.

Acid halides.—The chlorides of many metals absorb considerable quantities of hydrogen chloride, and at the same time much heat is evolved. This is supposed by M. Berthelot [13] to show that **acid chlorides** may be formed, but if so, M. Berthelot and L. de St. Martin consider that the products obtained with the monobasic acids are decomposed more or less completely when dissolved in water, since the thermal change which attends the admixture of one eq. quantity of hydrogen chloride with an eq. of potassium, sodium, or ammonium chloride varies from −0·03 to −0·04 cal.

The products with the dibasic acids are only partially decomposed, the degree of decomposition depending upon the relative proportions of water, acid, and neutral salt. In accord with the solubility law, the solubility of chlorides in conc. hydrochloric acid is generally less than in water, but in some cases, the solubility is greater. For instance, this is the case with mercuric chloride, and M. le Blanc and A. A. Noyes found the f.p. of soln. of mercuric chloride in hydrochloric acid to be progressively depressed only up to the point where the soln. contains the eq. of $HgCl_2.2HCl$.

There are similar indications of the formation of a number of other acid chlorides, $CuCl.HCl$; $FeCl_3.HCl.2H_2O$; $CuCl_2.2HCl$; etc.; and P. Pfeiffer (1902) has compiled the following list of acid chlorides which have been isolated: $CuCl.HCl$; $CuCl_2.HCl.3H_2O$; $CuCl_2.2HCl.5H_2O$; $CuCl_2.2HCl.HgCl_2.HCl$; $PtCl_2.HCl.2H_2O$; $PtCl_4.HCl$; $PtCl_4.2HCl.6H_2O$; $AuCl_3.HCl.4H_2O$; $ZnCl_2.HCl.2H_2O$; $2ZnCl_2.HCl.2H_2O$; $CdCl_2.2HCl.7H_2O$; $SnCl_2.HCl.3H_2O$; $SnCl_4.2HCl.6H_2O$; $2SbCl_3.HCl.3H_2O$; $2BiCl_3.HCl.3H_2O$. Similar remarks apply to the **acid bromides**, and P. Pfeiffer's list (1902) contained: $HgBr_2.HBr.4H_2O$; $CuBr_2.HBr.2H_2O$; $AuBr_3.HBr.5H_2O$; $IrBr_3.3HBr.3H_2O$; $SnBr_4.2HBr.8H_2O$; $PtBr_4.2HBr.8H_2O$; $TeBr_4.HBr.5H_2O$; $TeBr_3.HBr$. The **acid iodides** likewise comprise: $SnI_2.HI$; $PbI_2.HI.5H_2O$; $BiI_3.HI.4H_2O$; $PtI_4.2HI.9H_2O$; $TeI_4.HI.8H_2O$.

J. H. Kastle[14] has emphasized the fact that, excluding the colouring effects of the chromatic elements like chromium, nickel, copper, cobalt, etc., nearly all the fluorides are white, but a few are coloured—*e.g.* bismuth fluoride is reported to be grey. *The greater proportion of chlorides are white*, while but a few are yellow—*e.g.* phosphoric chloride, PCl_5. The bromides are generally white; several are yellow—*e.g.* silver bromide and phosphoric bromides—and a few are red—*e.g.* the polybromides, KBr_3; bromine hydrate, $Br_2.5H_2O$; tellurium bromide is orange. The iodides are usually white; many are a darker yellow than the bromides—*e.g.* silver, mercuric, mercurous, and lead iodides; a few iodides are red—*e.g.* polyiodides, KI_3; carbon tetraiodide; and phosphorous, arsenous, and mercuric iodides. Some of the polyiodides have a colour very like solid iodine—*e.g.* tellurium iodide is black. A gradation in colour is sometimes observed in passing from the fluoride or chloride to the iodide—*e.g.* silver fluoride is white, the bromide is pale yellow, and the iodide, yellow; phosphorus pentafluoride is colourless, the chloride is pale yellow, and the bromide is yellow—the iodide is not known. J. H. Kastle argues that the darkening of the colour of the halides with heat shows that a little dissociation is taking place, and hence infers that the darker colour of the iodides and bromides is also due to dissociation. The less stable the halide the more highly coloured the product. It is very doubtful if the first premise is right.

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§ 13. Colour Changes on Heating Elements and Compounds

Many observers[1] have noticed that the colour of several substances becomes darker when heated, and E. J. Houston said that the addition of heat causes a colour *to pass from one with a greater to one with a less vibration frequency.* In other words, the alterations in colour which substances undergo when heated is such that the colour passes through the chromatic scale

Heating→
White–Violet–Blue–Green–Yellow–Orange–Red–Brown–Black
←Cooling

The chromatic changes thus take place in a definite order, the order of the spectrum colours from the violet towards the red end of the spectrum and subsequently brown or black. The violet and blue stages are often omitted, and the colour changes directly from white to pale yellow. Table XVIII is cited in illustration.

TABLE XVIII.—COLOUR CHANGES OF COMPOUNDS WITH TEMPERATURE.

Compound.	Normal colour at ordinary temp.	Colour change with rise of temp.
Zinc oxide	White	Yellow to orange
Mercuric iodide	Red	Dark red
Lead oxide	Yellow	Orange to red
Thallium iodide	Yellow	Orange to red
Copper borate	Blue	Green to greenish-yellow
Lead chromate	Yellow	Red to black
Silver iodide	Yellowish-white	Orange, red, dark red
Mercuric oxide	Orange-yellow	Orange, red, brown

J. H. Kastle (1900) also noted that coloured substances usually become lighter in colour on cooling; thus, bromine at $-190°$ is orange-red, at ordinary temp. dark red; red phenolphthalein in alcoholic soln. becomes colourless; violet chromic chloride becomes pink; citron-yellow phosphorus pentabromide and yellow iodoform become white or pale yellow; red mercuric iodide becomes orange-yellow; rhombic sulphur becomes nearly colourless at $-190°$; red phosphorus, dark plum-coloured chromic alum, pink manganese chloride, and golden-yellow iodide become much paler in colour. I. Walz added that the same order is observed in a large number of reactions in which the colour change is induced by chemical action.

W. Ackroyd also found that the colour of compounds becomes redder when heated, and considered that the *metachromatism*, as he styled it, is due to an increased absorption of light with elevation of temp., so that the more refrangible rays increase at a greater rate than the less refrangible rays, a conclusion which was confirmed by measurements of E. L. Nichols and B. W. Snow with sulphur, molybdic acid, lead monoxide, red lead, mercuric iodide, mercuric oxide, mercuric sulphide, ferric oxide, chromic oxide, ultramarine, and zinc oxide. They showed that a pigment owes its colour to light reflected from the interior because that reflected from the surface is nearly white. When a pigment is heated, its reflecting power is diminished; and the diminution is usually more marked in the regions of the

greatest refrangibility. The changes in colour on heating are due to this unequal loss of reflecting power, and the colour appears to shift towards the red because the loss of brightness is least in the red and increases rapidly in passing towards the violet end of the spectrum as illustrated with sulphur in Fig. 18. There are, however, cases—*e.g.* chromic oxide and zinc oxide—where there is a shifting towards the longer wave-lengths. The converse change occurs on cooling. Thus, E. Wiedemann has shown that sulphur becomes white when cooled by carbon dioxide snow, and becomes more intensely yellow as the temp. approaches the m.p. The weakening or dilution of the colour is due to an increased reflecting power. W. Ackroyd assumed that as the absolute zero is approached, the prevailing tints of pigments will be blues and violets, merging finally into white.

W. Ackroyd and W. M. F. Petrie further showed that with binary compounds, an increase in the electronegative element produces a colour change towards the red end of the spectrum. Thus, mercurous iodide and chromic sesquioxide are green, while the corresponding mercuric iodide and chromium trioxide are red; aurous oxide is green, gold sesquioxide is brown; nickelous oxide is green, the sesquioxide is black; manganous oxide is green; and of the higher oxides, manganese tetroxide is reddish-brown, manganese sesquioxide is brownish-black, manganese dioxide is black. Lead monoxide is yellow, lead tetroxide is red, and lead dioxide is brown; ferrous oxide is white or yellowish, ferric oxide is red; antimony trioxide is white, the pentoxide is yellow; bismuth trioxide is yellow, the pentoxide is brown; chromous chloride is white, chromic chloride violet; cuprous oxide is red, cupric oxide is black; etc.

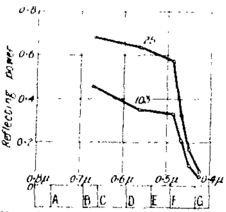

FIG. 18.—Reflecting Power of Sulphur at 25° and 103°.

T. Carnelley has further shown that if in a series of compounds A_nX_m, B_nX_m, C_nX_m, . . . in which A, B, C, . . . represent elements belonging to the same sub-group of Mendeléeff's Table, the colour passes wholly or partially through the series:

White→Violet→Blue→Green→Yellow→Orange→Red→Brown→Black

with an increase of the at. wt. of the elements A, B, C, . . . In other words, as the at. wt. of the elements A, B, C, . . . in the same sub-group of Mendeléeff's Table, increases, the more does the colour of a corresponding series of compounds pass towards the red end of the spectrum, and thence to brown and black. The rule does not necessarily apply to elements of the same group but a different sub-group; nor does the comparison apply if oxides are compared with sulphides, fluorides with chlorides, etc. For instance,

MgO	ZnO	CdO	HgO
White	White and yellow	Brown and red	Yellow and red

Of 426 cases tested, T. Carnelley obtained fifteen exceptions, and with these exceptions there is some doubt about the purity of the compounds whose colour has been reported, particularly with the salts of the rarer earths. There are also indications that the colours of the salts of the elements are periodic functions of the at. wt. In the case of the iodides when the ordinates represent the at. wt. of the positive element, and the abscissa a chromatic scale rising from black to brown, red, orange, yellow, green, etc., a periodic curve analogous with the at. vol. curve is obtained.

J. W. Capstick gives the following kinetic explanation of the phenomena: The molecules of a solid vibrate about certain mean positions, and with all the other conditions uniform, the period of vibration will be greater, the greater the mass of the molecule. If the period of vibration be small enough to coincide with some

vibration outside the violet end of the spectrum, no visible vibration will be absorbed, and the colour will appear white; when the mass of the vibrating molecule is augmented sufficiently to bring the period of vibration up to the violet end of the spectrum, the violet rays will begin to be absorbed, and the colour of the compound will appear to have the complementary tint—greenish-yellow; with a still further increase in the mass of the molecule, the blue rays will begin to be absorbed, and the light left unabsorbed gives the compound a yellow colour; the green rays are next absorbed, and the colour appears orange; yellow is then cut out and red remains; when the red is also cut out, the colour appears black. This shows at the same time how increasing the mol. wt. of the compound by atomic substitution or by introducing a greater quantity of the electronegative element can produce the same result. The results also show that when the period of vibration becomes great enough to cut out a particular colour, it also cuts all those of smaller wave-length—*e.g.* if yellow is cut out, then green and blue are also cut out; if otherwise, the colours would travel from orange to reddish-purple, and when the red is cut out the colour would incline to green instead of black. Some change of this character seems to occur with gold oxide, and the vanadium and uranium chlorides.

J. W. Capstick further explains the effect of temp. on the colour of compounds by assuming that (i) the molecules vibrate about certain mean positions, and that (ii) a rise of temp. produces a greater amplitude of vibration, but not a greater period, so that if the vibration be not quite harmonic, a greater amplitude may, as with a pendulum, require a longer period. (iii) A rise of temp. is also supposed to weaken the cohesion or inter-molecular attraction between the molecules, and thus lessen the force of restitution, so that the molecules vibrate more slowly and thus produce the same sequence of colour changes with rise of temp. as are observed when the mass of the molecule is increased.

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§ 14. Double and Complex Salts

Two or more simple salts, each primarily formed by the union of base and acid, may unite to form other salts—**compound salts**—of greater complexity, sometimes called **molecular compounds**. The compound salts are often well crystallized, and they are frequently formed by replacing one or more molecules of the water of crystallization by eq. molecules of another salt. Evidence concerning the state of a dissolved salt is mainly the result of observations on the physical properties of the soln.: *e.g.* rates of diffusion of the constituents, volume changes on mixing, thermochemical phenomena, solubilities, electrical conductivities, etc. If a soln. of two salts with common basic or acidic radicles be allowed to crystallize, (1) The salts may separate from the soln. independently, and upon this fact is based the process of fractional crystallization. (2) The two salts may crystallize simultaneously forming an isomorphous mixture—mixed crystals—in which the resulting crystals have a variable composition. The salts may be (*a*) miscible in all proportions; (*b*) partially miscible. (3) The two salts may separate in constant stöichiometrical proportions forming a double or complex salt. (4) Within certain

limits of concentration, both mixed crystals and double salts may be formed. There are three types: [1]

1. Mixed crystals and solid solutions.—Potassium perchlorate and potassium permanganate are isomorphous, and form mixed crystals of all shades of colour ranging from a faint pink to a deep purple according to the relative proportions of the two salts in the crystals. The physical properties of the mixed crystals are additive—that is, continuous functions of their compositions; and aq. soln. of the mixed crystals give reactions characteristic of their components—in the present example, of potassium perchlorate and potassium permanganate. The two salts form crystals containing all possible proportions between 100 per cent. potassium perchlorate and 100 per cent. potassium permanganate, as discussed under Retgers' law.

2. Double salts.—As in the case of mixed crystals, aq. soln. of double salts give reactions characteristic of the component simple salts, but the physical properties of the solid salt are not necessarily additive, and the component salts only unite in simple molecular ratios. For instance, soln. of colourless lithium chloride, LiCl, and green cupric chloride, $CuCl_2.2H_2O$, unite to form ruby-red crystals, and an aq. soln. gives reactions characteristic of chlorides, copper, and lithium; ferrous ammonium sulphate gives reactions characteristic of ferrous and ammonium sulphates. It is pure chance if the composition of a mixed crystal happens to be in simple molecular ratio since a variation in composition of the mother liquid from which the crystals are deposited will be attended by a variation in the composition of the crystals. A change in the composition of the liquid may change the composition of the compound salt, but the change will be abrupt, not gradual, in harmony with the law of multiple proportions.

3. Complex salts, or salts of complex acids. As in the case of double salts, the component salts of the so-called complex salts are combined in a simple molecular ratio, and the resulting compound salt is quite distinct from a mechanical mixture of the component salts; and unlike double salts, the chemical properties of a soln. of a complex salt are different from the properties of soln. of the component salts. Copper bromide forms a dark brown aq. soln., which becomes purple-red on the addition of lithium bromide; the change in colour is doubtless due to the formation of a complex $Li_2CuBr_4.6H_2O$. The term double salt is often applied somewhat loosely to compound salts formed by the union of one or more molecules of one salt with one or more molecules of another salt; but, as W. Ostwald [2] said in 1889, **the term double salt should not be applied to combinations of two salts which give reactions different from those of the constituent salts.** For example, the complex salt potassium ferrocyanide is a compound salt formed by the reaction: $4KCy+FeCy_2=K_4FeCy_6$. The product of this combination does not give the analytical reactions characteristic of potassium cyanide nor of ferrous cyanide. In the language of the ion theory, this is expressed by saying that **the ions of complex salts in solution are different from, and the ions of double salts are similar to, the ions of the simple salts from which they are derived.** The ions of potassium cyanide (neglecting secondary reactions) are $K^{\cdot}$ and Cy'; and the ions of ferrous cyanide, $Fe^{\cdot\cdot}$ and Cy'. The ions of potassium ferrocyanide, on the contrary, are $K^{\cdot}$ and $FeCy''''$. There are, therefore, no ions of Cy' and of $Fe^{\cdot\cdot}$ in an aq. soln. of potassium ferrocyanide. However, the term double salt and the corresponding formula are employed empirically—particularly when the character of the ions has not been established. According to the ion theory, the physical and chemical properties of dil. soln. of simple salts are in many cases the sum of the properties of the constituent ions; with complex salts, the physical and chemical properties—density, compressibility, capillarity, viscosity, refractive power, magnetic rotation, light absorption, colour, etc.—are usually very different from those of the ions of the constituent salts. In investigating the nature of a complex salt, physical and chemical methods may be applied, and, unless secondary changes intervene, the results furnished by each should be consistent with one another.

The rate of diffusion.—In order to find if the components of a double salt are dissociated in soln.—say, alum: $K_2SO_4.Al_2(SO_4)_{3aq.} \rightleftharpoons K_2SO_4 + Al_2(SO_4)_3 + Aq.$—T. Graham[3] assumed that the dissociated parts would diffuse with different velocities, and he found that potassium and aluminium sulphates diffused at different rates from an aq. soln. of potash alum into the pure solvent. Hence, he assumed that alum is partially dissociated into its constituents when in aq. soln. He likewise inferred that the components of the double sulphates of potassium and copper, and of potassium and magnesium, are not dissociated in aq. soln. since under the same conditions there is no sign of any difference in the rates of diffusion of the components. E. Fischer and E. Schmidmer[4] determined the relative quantities of the components of double salts which were drawn up by capillary attraction into rolls of filter paper. If a double salt is dissociated a larger proportion of the more diffusible component ascends the paper. Dissociation is far more pronounced in aq. than in alcoholic soln.

The specific volumes.—P. Kremers (1856)[5] and P. A. Favre and C. A. Valson (1873) argued that if the volume of a mixture of soln. of two salts in molecular proportions is equal to the sum of the volumes of the component soln. before mixing no double salt is formed in soln. Thus, it was inferred that potassium cupric sulphate does not exist as a double salt in aq. soln. and that the double salt must be born at the moment of crystallization. G. T. Gerlach, however, found that some salts behave in the converse way, and hence may be supposed to form complexes in aq. soln.

The heat of solution.—T. Graham (1844) and M. Berthelot (1883)[6] assumed that if the heat of soln. of a mixture of the constituents of a double salt is not equal to the heat of soln. of the double salt, the existence of the double salt in aq. soln. may be regarded as proved. For example, there is an evolution of heat when soln. of the halides of mercury and of potassium or ammonium are mixed toegther, but not when the corresponding sulphates are mixed. Hence, a double salt is formed in the one case and not in the other.

The rotation of polarized light.—Rotation of polarized light[7] is additive for soln. of mixtures of salts which do not form double salts, and there is a marked deviation from the additive law for mixtures known to form double salts.

The mutual solubility of two salts.—Numerous investigations have been made on this subject in the light of the phase rule by H. W. B. Roozeboom[8] and others. C. E. Linebarger also submitted mixtures of two salts to the action of various organic liquids in which one of the salts was insoluble. If both salts passed into soln. in a molecular ratio, it was assumed that a double salt is formed in soln. With a mixture of sodium and mercuric chlorides no double salt was formed with benzene or acetone as solvent, but with acetic ether, a salt, $(HgCl_2)_2NaCl$, was formed; similarly also with lithium and mercuric chlorides, the salt $HgCl_2.LiCl$ was formed; but no double salt was observed with potassium and mercuric chlorides in the same solvent.

The lowering of the freezing point.—F. M. Raoult (1884)[9] assumed that double salts are not formed in soln. when the lowering of the f.p. of the double salt is equal to the sum of the lowerings produced by the constituent salts. Thus the calculated value for the mixture $HgCy_2+2KCy$ is 9·50; the observed value for the double salt is 4·77. In J. H. van't Hoff's formula $i=1+(K-1)m$, where m denotes the fractional ionization, m and i can be substituted in the formula, and the corresponding values of K computed. E. Petersen (1897–1902) used this method for the cobalt, chromium, and platinum ammines. The calculation of m from the relation μ/μ_∞ is uncertain, because at extreme dilutions one of the complexes may be decomposed, and hydrolytic changes may occur. Too high a value for μ_∞ is also obtained if it is calculated as the sum of the molecular conductivities of the ions at infinite dilution. Hence, the value of K will be greater than that required. Values for the ratio u/v, for different dilutions, can be determined, and values of the transport numbers for the known ions introduced so as to calculate corresponding values for the complex ions

and for the maximum conductivity. This enables *m* to be calculated for fairly complex soln. when hydrolytic changes are not very marked.

The electrical conductivity.—E. Klein[10] showed that if there is a difference between the conductivity of a mixture of salts in soln. and the mean conductivities of the separate constituents, a double salt is probably formed. The molecular conductivity of a salt, and if possible of its components at different dilutions, has been employed to determine the number of component ions in a soln.; it was used, for example, by A. Werner (1893–1901) with the cobalt, chromium, platinum, and other ammines.[11] In moderately conc. soln. the double salts are but little ionized, and the difference between the conductivities of eq. soln. of potassium zinc chloride, $ZnCl_2.2KCl$, and of the sum of the constituents amounts to nearly 36 per cent., a value which is greatly in excess of that which would be due to the mutual influence of salts with a common ion. Tables of the molecular conductivities of salts show that with very few exceptions, at a dilution of 1024 litres and 25°, most salts have conductivities approximating those indicated in Table XIX.

TABLE XIX.—MOLECULAR CONDUCTIVITIES OF SALTS SOLUTIONS AT A DILUTION OF 1024 LITRES (25°).

Number of ions in the salts.	Examples.	Molecular conductivities of a dilution of 1024 litres.		
		Two fast ions.	One slow ion.	Two slow ions.
Two univalent ions .	KCl	150	120	85
Three ions . .	$BaCl_2$; Na_2SO_4	310	260	190
Four ions . .	K_3FeCy_6	480	420	380
Five ions . .	K_4FeCy_6	640	550	510

The ionic mobility of the simpler ion of a complex salt is usually known, and the other more complex ion will have a mobility, because, as W. Ostwald has shown, the mobility of an ion decreases as the number of constituent atoms increases. For example, dinitrotetramminecobalt chloride, $[Co(NH_3)_4(NO_2)_2]Cl$, furnishes two ions, the mobility of the chlorine ion is comparatively high, that of the other low.

The nature of the ions.—In 1814, G. F. Parrst[12] found that in the electrolysis of aq. soln. of potassium ferrocyanide the alkali accumulated about the negative pole, and ferric oxide and hydrocyanic acid about the positive pole, and the work of J. F. Daniell and W. A. Miller, and of W. Hittorf (1859), showed that double salts are of two kinds, and that in the one kind the metal is bound as a complex negative ion, and in the other it is the positive ion. For example, in the electrolysis of potassium silver cyanide, KCy.AgCy, W. Hittorf (1859) found that silver was deposited on the cathode, whereas with salts of the type $AgNO_3$ it is deposited on the anode. Hence, it was inferred that the salt ionizes $KAgCy_2 \rightleftharpoons K^{\cdot} + AgCy_2{}'$; similarly,

$$Na_2PtCy_6 \rightleftharpoons 2Na^{\cdot} + PtCy_6{}' ; \quad K_4FeCy_6 \rightleftharpoons 4K^{\cdot} + FeCy_6{}''''$$
$$NaAuCl_4 \rightleftharpoons Na^{\cdot} + AuCl_4{}' ; \quad K_3FeCy_6 \rightleftharpoons 3K^{\cdot} + FeCy_6{}''''$$

In establishing the character of a complex (or a double) salt, it is necessary to determine the nature and number of the constituent ions. It is usually simpler to determine if a given metal is in the positive or negative ion by investigating the changes of concentration of the liquid about the electrodes during electrolysis. Allowances have to be made for secondary changes.

The physical properties of a double salt in soln. may or may not be different from those of a simple mixture of the constituents, because complex salts may be completely, partially, or not at all dissociated into their constituent salts in soln.—dil. or conc. In the limiting case, the physical properties will be additively those of their components—complete dissociation—but in some cases, this is not the case. For instance, the solid double salt $FeCl_3.2KCl.H_2O$ is red.[13] A conc. aq.

soln. of the double salt, or of an eq. mixture of the component salts, at 15°, has the characteristic yellow tint of ferric chloride, $FeCl_3$, but at about 30° the yellow colour gives way to red. This is supposed to show that the double salt is not dissociated into its constituent molecules at 30°, but it is dissociated at 15°. Ferric chloride alone in soln. does not give the red colour at 30°. Similar remarks apply to many other physical properties of double salts. **A complex salt might dissociate into its component salts under certain conditions of temperature so that it acts as a dissociated double salt at one temperature, and as a complex salt at another.**

Double salts and isomorphism.—The tendency to form double salts is connected with certain differences in the character of the basic elements in the two salts. The sulphates of the zinc family: $RSO_4.7H_2O$, do not form double salts, nor do the sulphates of the potassium family, but there is a great tendency for a member of the one family to form double salts with a member of the other family. Again, the members of each family form a series of isomorphic mixed crystals among themselves, and the closer the chemical relationship the greater this tendency. This is shown by the continuous series of mixed crystals between zinc and magnesium sulphates. J. W. Retgers[14] even generalizes these facts, and asserts that two simple salts which form a continuous series of mixed crystals cannot form a double salt, and conversely. Isomorphism and combination, says he, are mutually exclusive. Potassium, rubidium, and cæsium form isomorphous mixtures, but not double salts; potassium and sodium are not isomorphous, and they form double salts—*e.g. Rochelle salt* or *Seignette salt* is a double potassium sodium tartrate, $NaKC_4H_4O_6.H_2O$, and *Scacchi's salt* is a double sodium ammonium racemate, $NaNH_4C_4H_4O_6.H_2O$. The sulphates and selenates are isomorphous, but they do not form double salts, while sodium nitrate unites with sodium sulphate to form a double salt. Similarly, the fact that silver and potassium form a series of double salts, but silver and sodium do not, is taken to indicate a closer relationship between silver and sodium than between silver and potassium, and this is confirmed by the isomorphism between the nitrates and the chlorates of silver and sodium. The greater the electrochemical difference between the constituents of a series of double salts, *the greater the stability of the resulting product. For instance, the cæsium* salts are the most stable of the alkali double salts in conformity with the fact that cæsium is the most electropositive of all the metals—F. W. Hinrichsen and E. Sachsel, for example, found that the stability of the double ferric alkali chlorides increases with the electropositive character of the alkali metal. No compound of sodium and ferric chlorides occurs between 0° and 60°, but with potassium chloride one double salt, $FeCl_3.2KCl.H_2O$, is formed, while cæsium chloride gives two such salts: $FeCl_3.2CsCl.H_2O$ and $FeCl_3.3CsCl.H_2O$.

The relation between the tendency of an element to form a complex and its position in the electrochemical series has also been emphasized by R. Abegg and G. Bödlander (1899);[15] **the tendency to form complexes increases with decreasing electro-affinity as measured by the decomposition potentials.** The stability of a complex is a measure of the tendency of its constituents to combine, and this is assumed to be the greater, the smaller the amount of complex ionized. The complexes formed by dissolving the mercuric halides in a soln. containing a common anion takes place according to the reaction: $m\mathrm{HgX}_2+n\mathrm{X}'=(\mathrm{HgX}_2)_m\mathrm{X}'_n$; the more stable this complex, the less will it be ionized: $(\mathrm{HgX}_2)_m\mathrm{X}'_n=m\mathrm{Hg}^{\cdot\cdot}+(2m+n)\mathrm{X}'$. G. Bödlander (1903) represents the stability of a complex by what he calls the **stability constant,** which he assumes is equal to the concentration of the complex divided by the product of the concentrations of the component ions raised to that power which, according to the law of mass action, corresponds to the number of single ions constituting the complex. For the above reaction, the stability complex is

$$\text{Stability complex} = \frac{(\mathrm{HgX}_2)_m\mathrm{X}'}{(\mathrm{Hg}^{\cdot\cdot})^m(\mathrm{X}')^{2m+n}}$$

The stability complex of the series of mercuric salts, $HgCl_2$, $HgBr_2$, $Hg(SCy)_2$, HgI_2, $HgCy_2$, increases in the order named.

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§ 15. Double Halides

Different metal chlorides unite with one another to form double salts. Just as the acidic and basic oxides unite together to form oxy-salts, so do the halides of an electropositive element (or radicle) unite with a halide of a less positive element (heavy metal or metalloid) to form double halides. So far as is known the alkali chlorides do not unite with one another to form double salts, nor do the halides of the same natural group form compounds with one another, but compounds of the alkali chlorides with the chlorides of the more electronegative chlorides are known. A comparison of nearly 500 double halides has been made by H. L. Wells (1901).[1] He calls the one component—*e.g.* the alkali halide—the *positive halide*, and the other the *negative halide*. A. Werner calls the halide which plays the *rôle* of the basic oxide, the *basic halide*, and the other, the *acid halide*. A great many of the simple types of the double salts predominate. Writing the number of molecules of the positive halide first, and the negative halide second, salts of the 2 : 1 and 1 : 1 ratios cover about 70 per cent. of the list of known double halides, and 4 : 1, 3 : 1, 3 : 2, 2 : 3, and 1 : 2 represent over 25 per cent. Two halides sometimes unite in several proportions—for instance, six cæsium mercuric halides have been reported where

$CsCl : HgCl_2=3:1$, $2:1$, $1:1$, $2:3$, $1:2$, and $1:5$; and five cæsium antimonious fluorides where $CsF : SbF_3=1:1$, $3:4$, $4:7$, $1:2$, and $1:3$. According to *I. Remsen's rule* (1889): When a halide of any element combines with a halide of an alkali metal to form a double salt, the number of molecules of the alkali salt which are added to one molecule of the other halide is never greater, and is generally less than the number of halogen atoms contained in the latter—for instance, in the double fluoride of sodium and aluminium, where the negative halide has three fluorine atoms, no more than three molecules of sodium fluoride will be found united with one of aluminium fluoride.

F. Ephraim (1903) also stated that the number of molecules of alkali halide which can unite with a heavy metal halide is greater (i) the smaller the at. wt. of the heavy positive metal; (ii) the greater the at. wt. of the negative metal; and (iii) the smaller the at. wt. of the halogen. He cited in illustration the fact that vanadium (at. wt. 51·2) forms a stable ammonium salt, $3NH_4F.VO_2F$, while the corresponding potassium, zinc, and copper salts are not known; but columbium (at. wt. 93·7) forms a potassium salt, but not the corresponding zinc and copper salts. F. Ephraim also showed that in the case of the vanadic fluoride and oxyfluoride, the number of the alkali fluoride radicles fixed in the molecule is determined by the at. wt. of the alkali metal or radicle. For example, the salts $6NH_4F.V_2F_6$; $5NaF.V_2F_6$; and $4KF.V_2F_6$; and $9NH_4F.VOF_2$; $8NaF.VOF_2$; $7KF.VOF_2$, have been made, while attempts to make $6NaF.V_2F_6$ have failed. H. L. Wells could find no indications dependent upon the positive or negative nature of the halide, and it follows that if the number of halogen atoms plays no part in the formation of these double salts, I. Remsen's rule cannot be valid. This is exemplified by the salts: $3CsCl.CuCl$; $4NH_4Cl.ZnCl_2$; $5TlI.TlI_3$; $2KCl.CuCl$; $4KCl.CdCl_2$; etc. It is therefore a mere accident that Remsen's rule applies to so large a proportion of the known double halides. Similarly, the double salts with rubidium and cæsium halides do not fit Ephraim's rule.

L. Meyer pointed out that the faculty of forming double compounds resides more particularly in the negative elements—*i.e.* the non-metals—and not in the positive elements—*i.e.* the metals. The negative elements exhibit a higher valency towards each other than positive elements. The affinity of a negative element or radicle is rarely exhausted by direct union with a positive element, and consequently these elements or radicles possess a surplus or residual affinity. The elements which are usually supposed to possess a feeble affinity for one another, manifest the greatest tendency to form double compounds. The relative stability of the halogens at high temp. as well as their general properties shows that in the series: Chlorine, bromine, iodine, cyanogen; chlorine has the greatest and cyanogen the least affinity for one another, and yet mercuric cyanide has a greater affinity for other cyanides than mercuric chloride or bromide for other chlorides or bromides respectively. Thus, according to J. Thomsen, the heats of formation of those compounds with the corresponding potassium halides in aq. soln. are: $HgCl_2.2KCl$, $-1·38$; $HgBr_2.2KBr$, 1·64; $HgI_2.2KI$, 3·45; $HgCy_2.2KCy$, 8·83 Cals. Similarly, the compound PI_3HI is more stable than the corresponding $PBr_3.HBr$ or $PCl_3.HCl$. The tendency of the different halides to form double salts is not always that which might have been anticipated; while some form typical double chlorides, bromides, and iodides, others form double chlorides, but not double bromides or iodides, etc.

Univalent halides—*e.g.* $NH_4Cl.AgCl$; $CsCl.CuCl$; $2KCl.CuCl$; etc. The halides of the alkali metals do not often unite together to form stable complexes. Univalent copper, silver, and gold form double chlorides with the alkali halides, while the corresponding double bromides of silver and gold and the double iodide of silver have not been made: The facts can be summarized in the form of a scheme due to P. Pfeiffer (1902), where the hyphens represent compounds which have not yet been prepared:

Cl	Cu	Ag	Au
Br	Cu	—	—
I	Cu	Ag	—

The ammonium salts seem to form a special series of a different type to most of the other salts. This is connected with the general tendency of ammonium salts to form complex compounds, which in turn depends upon the peculiar properties of nitrogen—the mercury-ammonia compounds can be cited in illustration. Similar remarks apply to the ferro- and ferri-cyanides, etc.

Bivalent halides.—These halides include those of beryllium, mangesium, zinc, cadmium, mercury, copper, lead, tin, platinum, palladium, etc. They could be subdivided into at least two classes typified (i) by $KCl.MgCl_2$; and (ii) by $2KCl.MgCl_2$; $2NH_4Cl.CuCl_2.2H_2O$, etc. P. Pfeiffer represents known and unknown compounds by the scheme:

Cl .	Cu	Mg	Zn	Cd	Hg	Sn	Pb	Mn	Co	Ni	Fe	Pd	Pt	Mo	--
Br .	Cu	Mg	Zn	Cd	Hg	Sn	Pb	Mn	Co	Ni	-	Pd	Pt	--	--
I .	--	Mg	Zn	Cd	Hg	Sn	Pb		Co	--	--	—	Pt	--	Ir

The double cupric, ferrous, manganous, and nickelous iodides have not been prepared; the double ferrous and molybdenous iodides are wanting; and the double iridious iodides have alone been prepared.

Tervalent metals. The halides of indium, thallium (ic), aluminium, iron (ic), manganese, arsenic, antimony, gold, chromium, rhodium, ruthenium, osmium, bismuth, etc., form at least three classes of salts typified by (i) $KF.BF_3$; $KCl.CrCl_3$; etc.; (ii) $2KI.BiI_3$; etc.; and (iii) $3NaF.AlF_3$; $3TlCl.FeCl_3$; etc. Fourteen give the double chlorides; while the double bromides and iodides of indium, manganese, rhodium, osmium, and ruthenium, and the double iodides of iron and of chromium are wanting. P. Pfeiffer gives the scheme:

Cl .	Al	In	Tl	Cr	Mn	Fe	Au	As	Sb	Bi	Ru	Os	Rh	Ir
Br .	Al		Tl	Cr		Fe	Au	As	Sb	Bi	-	-	-	Ir
I .	Al	.	Tl	-	-	--	Au	As	Sb	Bi	-		-	Ir

Quadrivalent metals.—This group includes ruthenium, palladium, osmium, platinum, tin, lead, tellurium, selenium, uranium, titanium, germanium, zirconium, thorium, manganese, antimony, etc. There are at least three types of salts represented by (i) $PtCl_4.2KCl$; (ii) a few of the type $SiF_4.LiF$, and (iii) $ZrF_4.3KF$. Selenium gives the double bromide; ruthenium, palladium, manganese, and antimony give the double chlorides; while osmium, uranium, tin, titanium, and thorium double iodides are wanting.

Cl .	Ir	Ru	Pd	Os	Pt	Sn	Pb	Te	--	U	Ti	Th	Mn	Sb
Br .	Ir		-	Os	Pt	Sn	Pb	Te	Se	U	Ti	Th	—	--
I .	Ir		-	.	Pt	--	Pb	Te	—	—	--	--	—	—

Salts of the 2 : 1 type with quadrivalent platinum are specially numerous.

Quinquevalent metals.—A few representatives of each of the following five classes are known: (i) $AsF_5.KF$; (ii) $AsF_5.2KF$, $2RbF.TaF_5$; (iii) $NbF_5.3KF$; (iv) $PCl_5.2SnCl_2$, $4NH_4Cl.SbCl_5$; (v) $PCl_5.SbCl_5$.

In a general way (1) the double halides increase in stability, ease of formation, and variety from iodides to the fluorides; (2) cæsium appears to form a more extensive series of double salts than any of the other alkali metals, but there are exceptions, for potassium and ammonium magnesium chlorides are easier to make than the corresponding cæsium salts; (3) *Godeffroy's rule* that all double salts of cæsium are less soluble than those of the other alkali metals is true in many cases, but it is not invariable, because the 1 : 1 cæsium zinc salts are too soluble to crystallize readily, while the corresponding potassium and ammonium salts are not difficult to crystallize. (4) The tendency of the double halides with the metals of the zinc family—magnesium, zinc, cadmium, and mercury—to form double halides increases with the at. wt., but it is doubtful if the rule applies generally—as exemplified by the zirconium, thorium, antimonious, and bismuth salts. (5) The gradation in the water of crystallization of the double halides, says I. Remsen, seems to increase

with the at. wt. of the halogen and decrease with the at. wt. of the alkali metal—for instance, there is generally a larger amount of water of crystallization in the sodium, and lithium salts, and in the iodides; and a smaller amount in the cæsium salts and in the fluorides. There are, however, some apparent exceptions to this rule. There is no evidence to show that a molecule of water of crystallization is eq. to an alkali halide molecule, similar to the relation supposed to subsist between $FeSO_4.7H_2O$ and $FeSO_4(NH_4)_2SO_4.6H_2O$.

The main difficulty in preparing the double halides rests on the ease with which they are decomposed by water, and the ease with which one halogen salt is decomposed by the acid of the other. Some success has been obtained in the employment of non-aqueous soln. for the preparation of salts which are decomposed by water. It is probable, too, that many of the double salts which have been reported are merely mixtures. For example, the so-called mixed double halides are probably mixtures of different double halides each containing one halogen. The evidence for the alleged double salt $PbI_2.4KI$ is now regarded as inadequate; and generally a re-examination of systems in the light of the phase rule has shown that many of the old data are quite unreliable—mixtures have been reported as double salts and *vice versâ*. Before the phase rule had been accepted as a guide, analyses of precipitates, etc., were interpreted by chemical formulæ, and no other check was employed. The double halides are usually prepared by bringing together the halogen salts in a strongly acid soln.; and the fact that they must usually be made in the presence of one of the halogen acids, limits the resulting product. For instance, a soln. containing both a bromide and a chloride would, in the presence of an excess of hydrochloric acid, form free hydrobromic acid and chloride only. In some cases the double halide can be made by bringing together the vapour of the one in contact with the other at a high temp.—*e.g.* the alkali aluminium chlorides.

Some metal hydroxides are said to have acidic properties developed by contact with strongly basic hydroxides, for these acidic hydroxides—aluminium, chromium, lead—form salts only with the stronger bases. The zincates, aluminates, chromates, plumbates, etc., may be cited in illustration. Similar remarks apply to the double halides—aluminium chloride, for example—which form double chlorides only with those chlorides which have strongly marked basic or acidic properties, and, with the exception of the zincates, I. Remsen argues that there is a formal analogy between the composition of the double halides and the oxy-salts—*e.g.* $NaAlO_2$ is parallel with $NaAlCl_4$; $AlPO_4$ with $AlPCl_8$; $KCrO_2$ with $KCrCl_4$; etc. Hence, just as there are acidic and basic oxides, so there are acidic and basic halides. In 1826 P. A. von Bonsdorff[2] and P. F. G. Boullay independently emphasized this idea, which was not favoured by the leading authorities J. von Liebig (1827) and J. J. Berzelius (1829). The idea was taken up by R. Hare (1840), who recognized the close analogy between the halides, the oxides, and the sulphides, so that whatever be the power which makes two oxides of opposite chemical characters unite and form a neutral salt, this power also exists with the halides; and, just as the acidic oxides unite with water to form hydrogen salts or acids, so do some of the acidic halides unite with the halide acids to form more complex acids. Compare the reaction: $CO_2+H_2O=H_2CO_3$ with $SiF_4+2HF=H_2SiF_6$; etc. Thus, the halogen acids bear the same relation to the double chlorides that water bears to the oxygen salts, and a halogen system of chemistry can be elaborated analogous with the more familiar oxygen system, which is even more striking than the analogy between the oxy- and the sulpho-salts.

The act involved in the formation of the double halides is the same as that involved in the formation of the oxygen salts, and the products in the two cases are of the same general character; two halogen atoms acting together in the double halides, play the same part as one oxygen atom in the oxygen salts. A. Naquet (1867) and W. Gibbs (1867) used this idea to explain the constitution of the double halides; the latter supposed potassium in the acid salt, HF.KF or HKF_2, and in the analogous KOH, to be tervalent. C. W. Blomstrand, in 1869, gave a more probable

explanation. He supposed the halogen to be tervalent, and explained the constitution of $MgCl_2.KCl$ by the formula $Cl.Mg.Cl : Cl.K$, and of K_2PtCl_6, by

$$\begin{matrix}Cl \\ Cl\end{matrix}>Pt<\begin{matrix}Cl=Cl-K \\ Cl=Cl-K\end{matrix}$$

C. W. Blomstrand even assumes that three chlorine atoms can unite together forming a tervalent group; and, with this hypothesis, the constitutions of the compounds $CuCl.2KCl$ (or $Cu_2Cl_2.4KCl$); K_4CdCl_6; and KBF_4 can be represented:

$$Cu-Cl-Cl-Cl<\begin{matrix}K \\ K\end{matrix}\,;\quad \begin{matrix}K-Cl \\ K-Cl\end{matrix}>Cl-Cd-Cl<\begin{matrix}Cl-K \\ Cl-K\end{matrix}\,;\ \text{and}\ \begin{matrix}F \\ F\end{matrix}>B-F=FK$$

The hypothesis that two chlorine atoms can form a bivalent group (either $-Cl=Cl-$ or $-Cl-Cl-$), was used to explain the constitution of chloroplatinic acid by S. M. Jörgensen (1877), and by J. W. Mallet (1881) to explain the formation of the double fluorides; and by J. F. Heyes to explain the structure of the double halides. In 1889, Ira Remsen showed that the structure of most of the double halides can be explained on the hypothesis that the halogen atom has the power to unite with itself to form a bivalent group which can take the place of one oxygen atom in the oxygen salts.

The various double halides can be regarded as complex salts derived from corresponding complex acids. For example, the salt $KCl.AuCl_3$ is regarded as a complex salt, $KAuCl_4$, derived from the complex acid, $HAuCl_4$; and $2AuCl_3.KCl$ is regarded as a complex salt, KAu_2Cl_7, derived from the complex acid, HAu_2Cl_7. A. Werner calls these acids *halogeno-acids*, and the corresponding salts *halogeno-salts*. According to his system, the chlorides: BF_3KF; $CdCl_2.4KCl$; $CuCl.2KCl$, and $PtCl_4.2KCl$, are graphically symbolized:

$$\left[\begin{matrix}F & & F \\ F & \vdots B \vdots & F\end{matrix}\right]K \qquad \left[\begin{matrix}Cl & & Cl \\ Cl & \vdots Cd \vdots & Cl \\ Cl & & Cl\end{matrix}\right]K_2 \qquad \left[Cl.Cu\begin{matrix}Cl \\ Cl\end{matrix}\right]K_2 \qquad \left[\begin{matrix}Cl & & Cl \\ Cl & \vdots Pt \vdots & Cl \\ Cl & & Cl\end{matrix}\right]K_2$$

where the halogen atoms of the basic halide are bound to the central atom, so that the acidic halide with the halogen atoms of the halide act as an acid anhydride. The names of the double halides are accordingly altered to suit the name of the corresponding acids—which may or may not have been isolated. The salt K_2SiF_6 is hence called potassium fluosilicate, and the corresponding acid, H_2SiF_6, hydrofluosilicic acid; Na_3AlCl_6 is sodium chloroaluminate, similarly with the chloraurates, iodoplumbates, chlorozincates, chloromagnesates, iodohydrargyrates, etc. It is, however, also customary to speak of Na_3AlCl_6 as the double chloride of sodium and aluminium, etc. According to A. Werner's nomenclature, $[ZnCl_5](NH_4)_3$ is ammonium pentachlorozinciate; $[FeCy_6]Na_3$ is sodium hexacyanoferriate; $[SbCl_6]Cs$ is cæsium hexachlorostibanate; and $[MnF_6]K_2$ is potassium hexafluoromanganoate.

A. Werner also includes the ammino-compounds or addition compounds of the halides with ammonia, and also compounds of the halides with water. Thus, the compounds $PtCl_4.2NH_3$; $PtCl_2.2NH_3$; and $PtCl_4.2H_2O$ are respectively symbolized:

$$\left[Pt\begin{matrix}Cl_4 \\ (NH_3)_2\end{matrix}\right] \qquad \left[Pt\begin{matrix}Cl_2 \\ (NH_3)_2\end{matrix}\right] \qquad \left[Pt\begin{matrix}Cl_4 \\ (OH)_2\end{matrix}\right]H_2$$

The mixed halogeno-salts are represented:

$$\left[Tl\begin{matrix}Br_3 \\ Cl_3\end{matrix}\right]Tl_3 \qquad \left[Tl\begin{matrix}Br_4 \\ Cl_2\end{matrix}\right]Tl_3 \qquad \left[Hg\begin{matrix}Cl_2 \\ Br_2\end{matrix}\right] \qquad \left[Pt\begin{matrix}Cl_4 \\ Br_2\end{matrix}\right]K_2 \qquad \left[Hg\begin{matrix}Br_2 \\ Cl\end{matrix}\right]Cs$$

E. Defacqz [3] prepared fluo-chlorides, fluo-bromides, and fluo-iodides of calcium, strontium, and barium—*e.g.* $CaF_2.CaCl_2$; SrF_2SrCl_2; $CaF_2.CaBr_2$; $SrF_2.SrBr_2$; $BaBr_2.BaF_2$; etc. Compounds of iodine trichloride with the metal chlorides have been prepared by R. F. Weinland and F. Schlegelmilch, and E. Filhol; antimony

fluoroiodides—$(SbF_5)_2I$ and SbF_5I—and bromochlorides have been prepared by O. Ruff: and compounds of the iodides with sulphur dioxide by E. Péchard. Compounds of metallic chlorides with phosphorus pentachloride, PCl_5; phosphoryl chloride, $POCl_3$; selenium oxychloride, $SeOCl_2$; and pyrosulphuryl chloride, $S_2O_5Cl_2$, are known. Many metal oxides and hydroxides unite with their respective halogen salts to form stable and definite oxychlorides, oxybromides, and oxyiodides.

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§ 16. Perhalides or Polyhalides

When iodine is dissolved in hydriodic acid or a soln. of a metallic iodide, there is much evidence of chemical combination, with the formation of a periodide. A. Baudrimont objected to the polyiodide hypothesis of the increased solubility of iodine in soln. of potassium iodide, because he found that an extraction with carbon disulphide removed the iodine from the soln.; but S. M. Jörgensen showed that this solvent failed to remove the iodine from an alcoholic soln. of potassium iodide and iodine in the proportion $KI : I_2$, and an alcoholic soln. of potassium iodide decolorized a soln. of iodine in carbon disulphide. The hypothesis seemed more probable when, in 1877, G. S. Johnson isolated cubic crystals of a substance with the empirical formula KI_3 by the slow evaporation of an aqueous-alcoholic soln. of iodine and potassium iodide over sulphuric acid. There is also evidence of the formation of analogous compounds with the other halides. The perhalides or polyhalides—usually polyiodides—are products of the additive combination of the metal halides, or the halides of other radicles with the halogen, so that the positive acidic radicle consists of several halogen atoms. The polyiodides have been investigated more than the other polyhalides. The additive products have often a definite physical form, and definite physical properties. J. J. Berzelius appears to have made the first polyiodide—which he called ammonium *bin-iodide*; A. Geuther called these compounds *poly-iodides*; and S. M. Jörgensen, *super-iodides*. They have been classified [1] as

(1) Metal periodides—*e.g.* G. S. Johnson's potassium and ammonium tri-iodides; etc.

(2) Iodonium periodides—*e.g.* C. Hartmann and V. Meyer's diphenyliodonium iodide, $(C_6H_5)_2I_2$; etc.

(3) Sulphonium periodides—*e.g.* J. H. Kastle and H. H. Hill's periodides of the benzene sulphonates; etc.

(4) Periodides of the nitrogen family of elements including:

(i) Alkylammonium bases—*e.g.* A. Geuther's tetraethylammonium heptaiodide, $N(C_2H_5)_4I_7$; tetramethylammoniumennaiodide, $N(CH_3)_4I_9$; etc.

(ii) Phosphonium and alkyl phosphonium bases—*e.g.* S. M. Jörgensen's tetraethyl phosphonium tri-iodide, and O. Masson and J. B. Kirkland's triethyl phosphonium periodide; etc.

(iii) Arsenium and alkylarsonium bases—*e.g.* A. A. T. Cahour's tetraethylarsonium tri-iodide; etc.

(iv) Stibonium and alkylstibonium bases—*e.g.* S. M. Jörgensen's.

(v) Quinoline perhalide of F. W. Dafert; the perhalides of the vegetable alkaloids papaverine, hyoscine, atropine, hyoscyamine, etc., of B. Pelletier and others; the tri-iodide of caffonium of W. A. Tilden; etc.

When a relatively small proportion of bromine is dissolved in a soln. of hydrobromic acid, or a bromide, it is probable that a tribromide is formed—say HBr_3 or KBr_3—while if the soln. be sat. with bromine still higher bromides are formed. In the case of potassium bromide, for example, the soln. probably contains unknown amounts of KBr, KBr_3, KBr_5, and may be still higher forms. In 1829, C. Löwig[2] noted that soln. of the alkali bromides can dissolve relatively large amounts of bromine, and M. Berthelot showed that cold nearly sat. soln. of the chlorides of the alkaline earths dissolved relatively large quantities of bromine, presumably owing to the formation of perbromides—*e.g.* $BaBr_4$. F. Boericke also inferred that the relatively high solubility of bromine in potassium bromide soln. means that most of the bromine exists as KBr_3, although some penta- and hepta-bromide is probably also formed. This conclusion has been confirmed by the solubility determinations of F. P. Worley, and J. M. Bell and M. L. Buckley. W. Herz and W. Paul also obtained evidence of the formation of mercuric perbromide, $HgBr_4$, bromoiodide, $HgBr_2I_2$, and chloroiodide, $HgCl_2I_2$. A. F. Joseph and J. N. Jinendradasa found that when a soluble bromide—of hydrogen, sodium, and potassium—is added to bromine water, the colour decreases until the concentration has reached normal, when any further addition has very little effect on the colour. It is therefore assumed that the colour, at first due to free and combined bromine, is normal when the whole of the bromine is combined, and this corresponds with the formation of a tribromide.

Hydrogen perhalides.—The dark brown soln. which is obtained by dissolving iodine in hydriodic acid in aq. soln. contains an unstable **hydrogen periodide,** $HI.I_2$ or HI_3. The corresponding salts have been isolated—as polyiodides or periodides. Similar remarks apply to the dark red liquid obtained by dissolving bromine in hydrobromic acid—**hydrogen perbromide,** HBr_3. The heat of soln. of bromine in hydrochloric acid led M. Berthelot[3] to conclude that a **hydrogen chlorobromide**, $HClBr_2$, is formed. N. R. Rjewskaja's measurements of the vap. press. of soln. of bromine in hydrobromic acid led to a similar conclusion, and that a certain proportion of the bromine is in the form of an emulsion. E. H. Büchner and B. J. Karsten found no indication of any compound in the f.p. curve of liquid hydrogen bromide and bromine; there is a eutectic at $-95°$ with a mixture containing five molecules of bromine to one of bromide; hence it is concluded that the hydrogen bromide and bromine unite together only in the presence of ionizing solvents, not in non-ionizing solvents. The increased solubility of chlorine in hydrochloric acid has also led to the suggestion that a **hydrogen perchloride,** HCl_3, is formed in aq. soln. corresponding to the behaviour of iodine in hydriodic acid.

N. A. E. Millon[4] found that when lead dioxide, PbO_2, is added to well-cooled and conc. hydrochloric acid, but little chlorine is evolved, while lead chloride, $PbCl_2$, and a yellow liquid are formed. The liquid slowly evolves chlorine and contains lead in soln. Lead dioxide is precipitated when water is added to the yellow liquid. It was therefore assumed that the liquid contains *lead perchloride*, $PbCl_4$, in soln.; and A. Guyard supposed that a soln. of iodine in potassium iodide contained *potassium di-iodide*, KI_2, because this soln. gives *lead tetraiodide*, PbI_4, when treated with a lead salt.

A study of the lowering of the f.p. of soln. of iodine in potassium iodide or other iodides of the alkalies of alkaline earths, led M. le Blanc and

A. A. Noyes[5] to the belief that the number of molecules in the soln. is not changed by the addition of more iodine because polyiodides are formed: $MI+nI_2=MI_{2n+1}$. Y. Osaka showed that the rise of the f.p. which occurs when iodine is added to hydriodic acid or to aq. soln. of potassium iodide is proportional to the amount of iodine added, and is greater for hydriodic acid than for the potassium salt. Hence, the total concentration of the ions and of unionized molecules is decreased by the addition of iodine. A. A. Jakowkin inferred from the partition coeff. of iodine in dil. soln. that potassium tri-iodide was formed, and that with more conc. soln. still more complex polyiodides are produced. Still further, the change in the partition coeff. of iodine between aq. soln. of potassium iodide and nitrobenzene led H. M. Dawson and R. Gawler to infer that polyiodides as high as potassium ennea-iodide, KI_9, are probably present in soln., although no such compound has been obtained in the solid state. H. L. Wells and H. L. Wheeler and others, however, have prepared several solid alkali polyiodides; for example:

Trihalides.—KI_3; RbI_3; CsI_3; $KICl_2$; $CsICl_2$; $Hg(I_3)_2$; etc.
Pentahalides.—$CsBr_5$; CsI_5; $Li(ICl_4).4H_2O$; $Na(ICl_4)$; $Ca(ICl_4)_2.8H_2O$; etc.
Heptahalides.—$N(CH_3.C_2H_5)_3I_7$; $N(CH_3)_2(C_2H_5)(C_6H_5)I_7$; etc.
Enneahalides.—$N(CH_3)_4I_9$; $N(C_2H_5)(CH_3)_3I_9$; etc.

The tri-iodides may be regarded as salts of the perhalogen acids, but no hydrogen compound corresponding with the higher polyiodides have been obtained.

A solvent in which iodine is very soluble is needed for the formation of the higher polyiodides. The lowest polyiodides are formed by saturating iodine soln. with potassium iodide, and the highest polyiodides by saturating potassium iodide soln. with iodine. According to F. Olivari,[6] the solubility of the polyiodides is greatest in solvents with the largest dielectric constant. Thus, ether, aniline, and the hydrocarbons dissolve no polyiodide, while the nitro-hydrocarbons—nitrobenzene, *o*- and *m*-nitrotoluene, *m*-nitroanisol, nitropentane—dissolve relatively large quantities, although they do not dissolve very much iodide. The highest polyiodide with ethyl alcohol, cyanide, acetate, and isobutyl alcohol is potassium ennea-iodide, KI_9; and with nitromethane, potassium hepta-iodide, KI_7.

The investigation of the equilibrium constant K in the reaction $KI+I_2\rightleftharpoons KI_3$ when

$$K_1=\frac{[KI][I_2]}{[KI_3]}; \quad \text{or} \quad K=\frac{[I'][I_2]}{[I_3']}$$

where the bracketed symbols represent concentrations in the one case according to the molecular and in the other according to the molecular hypothesis. The values of K have been determined by A. A. Jakowkin, H. M. Dawson, W. C. Bray and G. M. J. McKay, and others.[7] For dil. soln. of potassium iodide at 25° the value of K is nearly constant, 0.00136 ± 0.00005; and for conc. soln., at 25°, the value of K varies from 0.00150 to 0.00046. While for dil. soln. the constancy of K is in agreement with the assumption that the reaction is that postulated above, the deviation of K with the more conc. soln. is taken to show that the simple equation $KI+I_2\rightleftharpoons KI_3$ no longer applies, because higher polyiodides are formed in agreement with S. Baup's observation that iodine is precipitated when a conc. soln. of iodine and potassium iodide is diluted with water. From the condition of equilibrium $[KI][I_2]=0.00136[KI_3]$, it follows that in a soln. containing 0.00136 mol. of free iodine I_2 per litre, the concentration of the potassium iodide and tri-iodide will be the same. G. A. Linhart found for the equilibrium constants $[Br_3']=K_1[Br'][Br_2]$, and $[Br_5']=K_2[Br_3'][Br_2]$, the values

	0°	25°	26.5°	32.6°
K_1	19.6	16.1	15.9	15.5
K_2	2.08	1.23	1.20	1.07

The heat of formation: $I_{2\,solid}+I'_{aq.}=I_3'{}_{aq.}$ is −360 cals. at 5°; −2080 cals. at

18°; and −2780 cals. at 55°. According to G. N. Lewis and M. Randall, the free energy of formation of tri-iodide ion $I' + I_{2solid} = I_3'$, is −12216 cals. at 25°; for the tribromide ion, $Br' + Br_2 = Br_3'$, 25247 cals.; and for the pentabromide ion, $Br_3' + Br_2 = Br_5'$, 24400 cals. G. A. Linhart calculated for the heat of the reaction $Br' + Br_{2aq.} = Br_3'$, −1290 cals., and for $Br_3' + Br_{2aq.} = Br_5' - 3390$ cals. from the equation $\log(K_1/K_1') = Q(T_2 - T_1)/RT_1T_2$.

The specific electrical conductivity [8] K of soln. of potassium iodide and of similar soln. sat. with iodine expressed in reciprocal ohms is for soln. containing n milligram molecules per litre

Concentration, n	100	50	10	1
KI soln., $K \times 10^6$	13080	6737·5	1423	147·9
$KI + I_2$ soln., $K \times 10^6$	11490	5930	1260	131·7

The lowering of the conductivity is not attributed to a change in the degree of ionization of the soln., but rather to the decreased mobility of the anions during the change from I' to I_3'. At 25°, the mobility of the I'-ion is 76·5; and of the I_3'-ion, 41·6. The diffusion constant of I_3'-ions, according to E. Brunner, is 0·9 per sq. cm. per day at 20°, that is, approximately the same as that of free iodine. When iodine dissolves in potassium iodide soln., W. C. Bray and G. M. J. McKay calculate that there is an expansion of 0·2376 c.c. per gram of iodine or 60·31 c.c. per mol. of iodine per litre of soln. The colour of dil. soln. of potassium tri-iodide is yellowish-brown; which with increased conc. becomes very dark blue, almost opaque, in thin layers dark red.

In R. Abegg and A. Hamburger's experiments (1906) [9] a fairly conc. soln. of iodine in benzene was shaken with the alkali iodide; the latter is not perceptibly soluble in benzene. If two solid phases—iodine and iodide, or two iodides—are in equilibrium with a soln. of definite conc. of iodine, and monoiodide is gradually added, iodine will be withdrawn from the soln., but the conc. of the iodine in the soln. will remain constant because iodine will be taken from the higher solid polyiodide until the system will contain only one solid phase. Any further addition of the monoiodide will alter the conc. of the soln. until it is reduced to such an extent that a lower iodide makes its appearance, when the conc. of the soln. again remains constant. Hence it is possible to find the conc. of the iodide in equilibrium with the monoiodide and a constant conc. of iodine. Similarly, by gradually increasing the conc. of the iodine higher polyiodides are obtained until the limit of saturation for iodine is reached, when iodine and the highest attainable polyiodide form the two solid phases. The composition of the individual polyiodides is determined by analysis of the solid phases when the conc. of the iodine soln. is variable.

H. W. Foote (1903) studied the equilibrium in the system, cæsium iodide, iodine, and water. If there are four phases—two solid iodides, or a solid iodide and solid iodine, soln., and vapour—the system will be univariant, and if the temp. and press. be fixed the solubility of the mixture will have one definite value for any one temp. Since solubility varies but slightly with variations of press., the solubilities of the iodides under atm. press. will not differ appreciably. Starting with a soln. of cæsium iodide in water at a fixed temp., and adding sufficient iodine to combine with part of the cæsium iodide and form a polyiodide, the solubility will return one fixed value with successive additions of iodine until all the cæsium iodide is converted into the first polyiodide. With further additions of iodine, the solubility will change with the formation of a little of the next polyiodide, but it will preserve one definite fixed value as long as these two iodides are present. Hence, if the sat. solution retains a constant composition, it may be taken as proof that the solid iodides have not changed in composition without regard to their relative amounts; when the composition of the sat. soln. changes this may be taken as proof that one solid phase has changed. By suitably varying the quantities of iodine and cæsium iodide in different soln., and measuring the solubility of each, H. W. Foote found

that cæsium tri-iodide and cæsium penta-iodide are the only cæsium polyiodides which can exist in aq. soln. between −4° *and* 73°.

R. Abegg and A. Hamburger (1906) obtained evidence of the existence of KI_7, NH_4I_3, RbI_3, RbI_7, RbI_9, CsI_3, CsI_5, CsI_7, CsI_9. The tri-iodides of potassium, sodium, and lithium could not be obtained since their vap. press. at 25° appears to be greater than that of iodine itself. The vap. press. of the solid alkali polyiodides, whose existence has been demonstrated at 25°, is indicated in Table XX. The negative complexes I_3', I_5', I_7', and I_9' recall similar complexes in connection with the alkali polysulphides. The closer relation of potassium than sodium to rubidium is

TABLE XX.—VAPOUR PRESSURE OF SOLID ALKALI POLYIODIDES (IODINE UNITY).

	I_3	I_5	I_7	I_9
Li . . .	—	—	—	—
Na . . .	—	—	—	—
K . . .	—	—	0·61	—
NH_4 . .	0·053	—	—	—
Rb . . .	0·026	—	0·63	0·73
Cs . . .	0·003	0·16	0·16	0·51

shown by the formation of a heptaiodide of potassium but not of sodium or lithium. The tendency of the alkali metals to form polyiodides decreases with decreasing at. wt. from cæsium to lithium: Cs, Rb, NH_4, K, Na, Li, and the order of the solubility of the corresponding polyiodides increases in the same order; similar remarks apply to the solubilities of the monoiodides in water expressed in mol. of salt per 1000 grms. of water:

	Cs	Rb	NH_4	K	Na	Li
Monoiodides	2·7	7·1	11·5	8·4	11·5	12·3

F. Ephraim found that if T denotes the absolute temp. at which the vap. press. of the liberated halogen is equal to one atm., then for corresponding pairs of the cæsium and rubidium polyhalides, $T_{Cs}/T_{Rb}=1·12$; and, if v denotes the at. vol., $T v^{\frac{1}{3}}$ is the same for the two members of each series. Given the dissociation temp. of the cæsium compound, it is possible to predict the stability of the analogous rubidium compound. F. Ephraim extended the rule to the potassium compounds when the corresponding rubidium compounds are known.

C. K. Tinkler[10] found that neither a 0·001 N-soln. of iodine in water, chloroform, or alcohol, nor a dilute aqueous soln. of potassium iodide gave any spectral absorption bands, and only a little general absorption in the ultra-violet, the addition of various iodides—potassium, sodium, magnesium, barium, cadmium, aluminium, hydrogen, ammonium, or tetramethylammonium iodide—to a 0·001 N-aq. soln. of iodine gave two absorption bands and a considerable general absorption. The colour of the solution changed from reddish-brown to yellow, and similar spectra were obtained, probably because all the soln. contain the same ion, viz. I_3', and the tri-iodides of all these bases are accordingly assumed to exist in aq. soln. Similar evidence of the existence of **bromoiodides** corresponding with $HBrI_2$, and of **chloroiodides** corresponding with $HClI_2$, was obtained by adding iodine to hydrobromic acid or soln. of bromides, or to hydrochloric acid, or soln. of chlorides. C. K. Tinkler also found similar results to obtain with the bromides and chlorides forming **chlorobromides.**

The R. Kremann and R. Schoulz's f.p. curve[11] of mixtures of iodine with up to 50 per cent. of potassium iodide is indicated in Fig. 19. According to R. Kremann and R. Schoulz, the curve falls from the f.p. of iodine, 113°, to a eutectic at 76° with 20·5 mol. per cent. of potassium iodide; and there is also a eutectic at 77° corresponding with 50 mol. per cent. of potassium iodide. The curve rises to an

indefinite maximum between these two points. It is inferred that the maximum represents a compound $2KI.3I_2$, *i.e.* KI_4, in a highly dissociated state. This is an example of a f.p. curve, discussed by R. Kremann (1905), in which the maximum is very flat, and in which the eutectics solidify at about the same temp. owing to the dissociation of the compounds concerned. The m.p. of potassium tri-iodide reported at 38° is thought to be an error due to the presence of water. The f.p. curve does not therefore establish the existence of potassium polyiodides under these conditions. This, of course, does not preclude the existence of other polyiodides in aq. soln. or in equilibrium with soln. of iodine in other solvents. F. Olivari obtained no indication of a periodide in the f.p. curve of iodine and mercuric iodide; and if calcium periodide exists under these conditions, it must be greatly dissociated at the m.p. C. L. Parsons and H. P. Corliss[12] could find no evidence of the formation of solid polyiodides in aq. alcohol soln. of iodine in potassium iodide, from the rise of the f.p., the electrical conductivity, and diffusion phenomena. They attribute the increased solubility of iodine in soln. of an iodide to the high solvent power of the dissolved solid. Similar conclusions were drawn by C. L. Parsons and C. F. Whittemore, and by J. M. Bell and M. L. Buckley. Measurements of the rate of diffusion of soln. through agar-agar jelly give no evidence of the existence of polyiodides in dil. or conc. soln., because the potassium iodide and iodine diffuse independently of any assumed combination between the two.

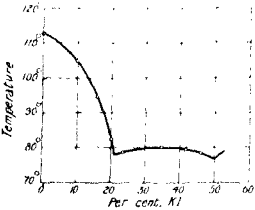

FIG. 19.—Freezing-point Curve of Iodine-Potassium Iodide.

A. Werner[13] regards thet rihalides as addition compounds, so that the trihalide $RICl_2$ becomes $[Cl.I.Cl]R$, dichloriodates on his system of nomenclature. The pentahalides are tetrachloroiodates analogous to the chloroauriates:

$$\left[\begin{array}{c} Cl \\ Cl\,.\,Au\,.\,Cl \\ Cl \end{array}\right]R \qquad \left[\begin{array}{c} Cl \\ Cl\,.\,I\,.\,Cl \\ Cl \end{array}\right]R \qquad \left[\begin{array}{c} I \\ I\,.\,I\,.\,I \\ I \end{array}\right]R$$

A. Werner says that the hepta- and enna-halides can be explained on the assumption that the co-ordination positions are occupied by iodine molecules. The non-existence of the tri-chlorides, says A. Werner, "is to be attributed to chlorine being unable to act as a central atom."

There is some doubt about the existence of **sub-halides**—sub-chlorides, sub-bromides, and sub-iodides—containing less halogen than corresponds normally with a monobasic acid—Ag_2Cl, AgBr, etc.

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CHAPTER XIX

THE OXIDES AND OXYACIDS OF CHLORINE, BROMINE, AND IODINE

§ 1. Chlorine Monoxide

NONE of the oxides of chlorine can be prepared by the direct union of the two gases, but several oxides have been prepared indirectly. They are all endothermal compounds. In this respect, the oxides of chlorine bear the same relation to hydrogen chloride that hydrogen peroxide does to water. Hydrogen chloride and water are formed from their elements with the loss of energy, and cannot therefore decompose spontaneously back into their elements, but hydrogen peroxide and the chlorine oxides are formed with an absorption of energy, and they are so unstable that they readily decompose spontaneously with the evolution of heat, and that sometimes with explosive violence. The halogen oxides are prepared by means of the so-called *gekoppelte Reaktionen*,[1] or **coupled reactions,** in which the energy required for their formation is obtained by the simultaneous production of other substances which liberate energy during their formation.

In order that the free energy of one reaction may be available for the production of an endothermal compound, it is necessary that the two reactions be dependent on or coupled with one another. If the two reactions are independent of one another, the free energy of the one reaction is not utilizable by the other, and it may act banefully by raising the temperature of the system. If the chemical equation representing the two processes can be resolved into two independent parts, the reactions are not coupled—*e.g.* the reaction symbolized : $3H_2+2O_2=2H_2O+H_2O_2$, can be resolved into the two independent processes : $2H_2+O_2=2H_2O$ and $H_2+O_2=H_2O_2$, for the one reaction is not conditioned by the other.

When chlorine acts on mercuric oxide, HgO, brownish-yellow mercuric oxychloride, Hg_2OCl_2, and chlorine monoxide, Cl_2O, are formed : $2HgO+2Cl_2=Hg_2OCl_2+Cl_2O$. In his *Recherches sur la nature des combinaisons décolorantes du chlore*, A. J. Balard [2] first described the preparation of the gas by this reaction in 1834. J. L. Gay Lussac filled a dry flask with dry chlorine, and introduced a test tube filled two-thirds with a mercuric oxide and the remainder with sand. The flask was closed and then well shaken. In a few minutes, the chlorine gas was converted into half its volume of chlorine monoxide.

According to J. Pelouze, chlorine monoxide is prepared by passing a slow current of cold and dry chlorine from the apparatus, *AB*, Fig. 1, through a glass tube, *C*, containing a layer of cold and dry precipitated mercuric oxide which has been previously heated for about an hour between 300° and 400°. Ground-glass joints form the connections between *C* and *D*. The tube *C*, which is about half a metre long, is cooled by immersion in cold water, and the issuing gas is passed through a U-tube, *D*, cooled by a freezing mixture to about −20°. The gas condenses in the U-tube to a reddish-brown liquid. If freshly precipitated mercuric oxide be used, the chlorine acts too vigorously, forming mercuric chloride and liberating oxygen—maybe explosively. To reduce the violence of the reaction J. L. Gay Lussac recommended mixing the mercuric oxide with sand, or potassium sulphate. If the mercuric oxide be in coarse fragments, or if it be the crystalline variety prepared by the oxidation process, the reaction is too slow. According to

G. Lunge and P. Naef, if the tube C contains a layer of mercuric oxide about 25 metres long, the issuing gas will contain 85 to 100 per cent. of chlorine monoxide, and be almost free from chlorine. For demonstration purposes, V. Meyer recommends collecting the heavy gas by the upward displacement of air.

The properties of chlorine monoxide.—Chlorine monoxide is a pale orange-yellow gas with slight greenish tinge. Its smell is not unlike that of chlorine, but the two are easily distinguished. The vapours attack the eyes and mucous membranes. The vapour density determined by J. Pelouze is 2·977, air unity; and according to K. G. Thurnlackh and G. Schacherl, 3·007. The gas readily condenses to a reddish-brown liquid, which boils about 5° under 738 mm. press. Chlorine monoxide was found by S. Goldschmidt to boil at 3·8° and 766 mm. According to J. Pelouze, the liquid is very unstable and explodes very readily when shaken or poured; but according to S. Goldschmidt, the liquid can be kept an indefinite time, at −80°, without decomposition. K. G. Thurnlackh, however, was able to distil the liquid, and he attributed the various reports of its explosibility to the presence of traces of organic matter. K. Schäfer (1919), and D. Gernez[3] (1872), have measured the absorption spectrum of chlorine monoxide; the latter found that with layers a metre thick, the spectrum resembles that of chlorine peroxide with absorption bands in the blue, indigo, and violet. The heat of formation, according to J. Thomsen, is $Cl_2+O=Cl_2O-17\cdot929$ Cals., and according to M. Berthelot, −15·1 Cals. The heat of soln. in a large quantity of water is 9·4 Cals. per mol. Both the liquid and the gas are very unstable. According to J. L. Gay Lussac, the gas dissociates explosively by raising its temp. by electric sparks, and by exposure to light; but the last statement is denied by K. G. Thurnlackh and G. Schacherl, who found that the gas did not suffer appreciable decomposition during 15 minutes' exposure to the direct rays of the sun. One volume of water dissolves 200 volumes of the gas at 0°—*i.e.* about three-quarters of its weight. The soln. has a golden-yellow colour and behaves like an acid—hypochlorous acid, HClO. The reaction is symbolized $Cl_2O+H_2O=2HOCl$. Hence chlorine monoxide is also **hypochlorous anhydride.** Mere contact of the gas with many **oxidizable substances** is attended by a violent reaction—*e.g.* with paper, caoutchouc, turpentine, sulphur, potassium, phosphorus, finely divided charcoal, arsenic, antimony, and many carbon compounds, it reacts explosively. The metals form oxides, and chlorides or oxychlorides—**silver** forms silver chloride and free oxygen; **mercury** reacts slowly forming the oxychloride; arsenic forms the pentoxide and trichloride; although finely divided **antimony** spontaneously ignites in the liquid or gas, a lump of antimony retains its metallic lustre in the liquid. **Sulphur** forms sulphur dioxide and sulphur chloride, and, according to A. Wurtz,[4] with a soln. of sulphur in sulphur chloride at 10°, thionyl chloride, $SOCl_2$, is formed. According to P. Schützenberger, chlorine monoxide is absorbed by **sulphur trioxide**, forming red crystals of a mixed anhydride of sulphuric and hypochlorous acid: when a soln. of chlorine monoxide in liquid **sulphur dioxide** is removed from the freezing mixture, chlorine is evolved, and thick red liquid is formed—the mixed anhydride of sulphuric and hypochlorous acid. Carbon disulphide explodes with chlorine monoxide, forming, according to P. Schützenberger, thionyl and carbonyl chlorides; and according to A. J. Balard, carbon and sulphur dioxides, sulphur chloride, and free chlorine. A mixture of chlorine monoxide and **hydrogen** detonates when a flame is applied; and a mixture with **hydrogen sulphide**

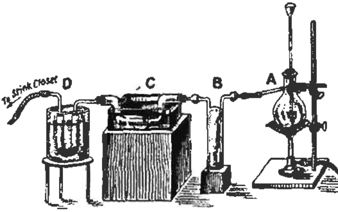

FIG. 15.—Preparation of Chlorine Monoxide.

or with **ammonia** also detonates. The gas exerts no action on **nitrous oxide. Hydrochloric acid** forms free chlorine and water: $Cl_2O+2HCl=H_2O+2Cl_2$. **Iodine** absorbs the gas, forming iodic acid and iodine chloride, and, according to P. Schützenberger, an orange-red oxychloride, $IOCl_3$, is formed. **Phosphine** detonates with chlorine monoxide; carbon monoxide forms phosgene and carbon dioxide. **Calcium phosphide** causes the gas to detonate, similarly with the sulphides of barium, tin, antimony, and mercury. Dry **calcium chloride** is not attacked by chlorine monoxide, but with the moist salt, calcium hypochlorite, $Ca(OCl)_2$, and chlorine are formed; and if the action is prolonged, calcium chlorate, $Ca(ClO_3)_2$, is produced.

The composition of chlorine monoxide.—A. J. Balard and J. L. Gay Lussac have established the composition of chlorine monoxide. Pass a stream of chlorine monoxide through a capillary tube with, say, three bulbs as indicated in Fig. 2. Heat the part of the tube just before the bulbs so as to decompose the gas before it enters the bulbs. The gas does not explode in the capillary tube. The bulbs can be sealed off at A, B, C, and D, and the contents of each analyzed. The exit tower is packed with lime and glass wool to absorb the excess of chlorine. The free chlorine in each bulb is absorbed by potassium hydroxide. The results show that two volumes of chlorine accompany every one volume of oxygen: $2nCl_2O=2nCl_2+nO_2$. Since, according to Avogadro's hypothesis, equal volumes of these gases contain the same number of molecules; and since both chlorine and oxygen have two-atom molecules, it follows that chlorine monoxide has two atoms of chlorine per one atom of oxygen; or the formula is $Cl_{2n}O_n$, where n has yet to be determined. The vapour density of chlorine monoxide is 86·92 ($H_2=2$). This corresponds with the molecule containing two atoms of chlorine and one atom of oxygen, and hence the formula of chlorine monoxide is written Cl_2O.

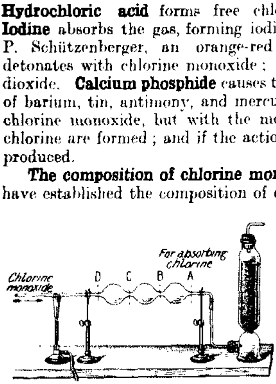

FIG. 2.—Charging Bulbs with decomposition products of Chlorine Monoxide.

J. L. Gay Lussac[5] thought that he had prepared *bromine monoxide*, Br_2O, by the analogous reaction between bromine and mercuric oxide, but W. Dancer showed that at 100° with an excess of dry mercuric oxide, a solid is obtained which bleaches like chloride of lime, and with an excess of bromine the resulting solid does not bleach. Much oxygen is given off in both reactions. The first-named product was supposed to contain some mercury hypobromite. Moist mercuric oxide and bromine furnish hypobromic acid at about 30°, or else decomposes into oxygen and bromine. Consequently, as H. Ditz has emphasized, there is no satisfactory evidence of the formation of bromine monoxide, or *hypobromous anhydride*, Br_2O. No corresponding iodine compound—*iodine monoxide* or *hypoiodous anhydride*, I_2O—is known.

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§ 2. The Preparation of Hypochlorous, Hypobromous, and Hypoiodous Acids

> The energetic action of chlorine on colouring matters which was to its discoverer Scheele merely an interesting experiment became to Berthollet the basis of a new art.—A. J. BALARD (1834).

Bleaching has been practised from ancient times; there are numerous allusions in the Scriptures to fine linen white and clean. Theophrastus (c. 300 B.C.) said that lime was employed in the operation; and there are numerous references in Pliny's *De naturalis historia* to the pre-eminence which white linen enjoyed, at Nero's court, for instance, it was esteemed above all other colours, and Pliny described how the Gauls and Britons of his time conducted the operation of bleaching. The goods to be bleached were spread in meadows, and thereby exposed alternately to moist and dry heat and cold, and to light and shade, until, after a long time—six, seven, or even eighteen months—they were perfectly bleached. C. T. Kingzett[1] thus describes the old operation:

> The goods were steeped in water or hot dil. alkaline lyes, after which they were boiled in similar soln., which operation was known as *bucking*. This done, the goods were exposed to the air on the grass—*crofting*—and after they had been exposed sufficiently long, they were immersed in sour milk—*souring*—and the whole operations repeated as often as was necessary.

In his memoir: *De magnesia nigra*, 1774, C. W. Scheele[2] pointed out that the chlorine water he discovered possessed the property of bleaching vegetable colours. He said:

> Paper coloured with litmus becomes nearly white; all vegetable red, blue, and yellow flowers likewise become white in a short time; the same thing happens to green vegetables. Meanwhile the water changes into weak but pure muriatic acid. The original colour of the flowers or of green vegetables could not be recovered either by the use of acids or alkalies.

In 1785, C. L. Berthollet conceived the happy idea of applying C. W. Scheele's discovery of the colour-destroying properties of chlorine for bleaching purposes, and mentioned the fact to James Watt of engineering fame. The facts were communicated by the latter to his father-in-law, a linen bleacher in Scotland. At that time, the Scotch bleachers were unable to produce so good results as were obtained in Holland and Flanders; and the best goods were shipped from Scotland to these countries to be bleached and returned to Scotland as white linen—*hollands*. J. Watt's father-in-law bleached 1500 yds. of linen with chlorine water; the results were surprisingly good; but the fabric rotted and was spoilt. The handling of the chlorine was also prejudicial to the workmen. James Watt communicated an account of the difficulty to C. L. Berthollet, who noticed that the addition of a little quicklime or even calcium carbonate or magnesia to the chlorine water used for bleaching, removed the penetrating and objectionable smell of chlorine from the aq. soln. without impairing its bleaching power. He showed that the objectionable after-effects could be avoided by the use of a soln. of chlorine in an alkaline lye; and that the soln. of the gas in potash lye—*chlorinated potash*—possessed great advantages in practice over the soln. of the gas in water. The alkaline liquid not only dissolved more gas than water alone, but it possessed a higher decolorizing power than an aq. soln. Manufacturers eagerly welcomed the new process, which in a few hours produced results which previously occupied several months. The new process, called the *Berthollean method*, was soon adopted, and chlorine passed, as A. J. Balard puts it, "from the laboratory of the chemist to the workshop of the arts." About this time, 1786, the new bleaching process was introduced in several works, and it was the subject of many patents.[3] In 1789 the bleaching liquor, known as *eau de Javelle*, was manufactured at the Quai de Javelle; and in 1820,

A. G. Labarraque[4] prepared the corresponding *chlorinated soda* by saturating soda lye with chlorine, and this was called *eau de Labarraque*. The term *eau de Javelle* is now often applied to both liquids.

The high cost of the alkalies employed in the manufacture of these bleaching liquids militated against the extensive application of the process; and in 1789, C. Tennant[5] patented the use of the much less costly lime, strontia, or baryta suspended in water in place of the alkali lye for "neutralizing the oxymuriatic acid." The patent was invalidated because of the prior use of milk of lime by the Lancashire bleachers for preparing *bleach-liquor*. In 1799, however, C. Tennant obtained another patent for the use of *dry* hydroxides of the alkaline earths, and commenced the manufacture of *bleaching powder* by saturating dry calcium hydroxide with chlorine gas. According to J. Mactear, in 1799–1800, 52 tons were made at a price of £140 per ton; in 1805, 147 tons at £112 per ton; in 1812, 333 tons at £60 per ton; in 1825, 910 tons at £27 per ton; and in 1870, 925 tons at £8 10*s*. per ton. The output in Great Britain in 1910 was 110,000 tons; and the world's output is over a quarter million tons.

In 1785, at the time when chlorine was thought to be a compound—oxymuriatic acid—C. L. Berthollet[6] attributed the bleaching properties possessed by a soln. of chlorine in the alkaline lye to the formation of a salt of oxidized muriatic acid—*muriates oxygénés*—in the liquor, but he was not very definite, for he added: *elle ne doit être reçue qu'avec le vague qui se trouve dans la combinaison elle-même.* J. J. Berzelius (1828) supposed the product of the action of chlorine on alkali lye to be a compound of the alkali chloride and chlorate; but in 1834, in his *Recherches sur la nature des combinaisons décolorantes du chlore*, A. J. Balard showed that the bleaching qualities of the chlorinated alkali lye were due to the presence of the alkali salt of a new acid. He said:

> The new acid is properly called *hypochlorous acid*, a name which recalls its analogy of constitution with hyposulphurous, hypophosphorous, and other acids formed like it of one eq. of their radicle and one eq. of oxygen. Its combinations are similarly called *hypochlorites*.

A. J. Balard prepared an aq. soln. of the acid, and isolated the anhydride—chlorine *monoxide*.

The preparation of the hypohalous acids.—The three hypohalous acids are hypochlorous acid, HOCl; hypobromous acid, HOBr; and hypoiodous acid, HOI. The work of A. A. Jakowkin[7] makes it highly probable that a *cold* aq. soln. of chlorine decomposes, forming a mixture of hydrochloric and hypochlorous acids. A. A. Jakowkin's equation is: $Cl_2+H_2O \rightleftharpoons HCl+HOCl$—a balanced reaction. This is evidenced by the fact that chlorine water reacts acid with litmus before it bleaches; and the more volatile **hypochlorous acid** can be separated by distillation. However, the amounts of the two acids present when the system is in equilibrium are very small. W. N. Haworth and J. C. Irvine patented the preparation of hypochlorous acid by passing chlorine through a series of bottles containing water together with a salt or oxide of copper, nickel, or cobalt to act as "catalyst"—80 to 100 grms. per 1·75 litres; with copper oxychloride only 10 grms. are needed. It is claimed that the product contains 2 per cent. of hypochlorous acid which can be freed from the dissolved copper by precipitation or distillation. If one of the products, say hydrochloric acid, be removed from the system: $Cl_2+H_2O \rightleftharpoons HCl+HOCl$, the equilibrium is disturbed and the reaction proceeds in the direction needed to re-establish equilibrium. If, for example, freshly precipitated mercuric oxide be present, the hydrochloric acid reacts with the mercuric oxide forming mercuric chloride, $HgCl_2$, or mercuric oxychloride, Hg_2OCl_2. The hypochlorous acid is such a weak acid that it has practically no action on the mercuric oxide. The action of chlorine on water containing mercuric oxide is therefore represented: $HgO+H_2O+2Cl_2 \rightleftharpoons HgCl_2+2HOCl$, or $2HgO+H_2O+2Cl_2=Hg_2OCl_2+2HOCl$. This process was employed by A. J. Balard.[8] The clear liquid can be distilled, the

hypochlorous acid collects in the first portion of the distillate. S. Reformatzky's directions for preparing the acid are :

Chlorine, derived from a mixture of hydrochloric acid and potassium bichromate in a 1500 c.c. flask, is washed in water, and then led into a 500 c.c. flask containing mercuric oxide covered with five times its volume of water. The flask is fitted with a stopper carrying an inlet tube reaching nearly to the bottom, and an exit tube connected with a fume chamber. This flask stands in water cooled with ice. When the reaction is nearly completed, the mercuric oxide disappears. The flask is agitated periodically. The soln. of hypochlorous acid mixed with mercuric oxide, etc., is distilled; the receiver should be connected with the fume chamber.

J. S. Stas employed silver carbonate in place of mercuric oxide : $Ag_2CO_3+2Cl_2+H_2O \rightarrow 2AgCl+CO_2+2HOCl$. M. Martens used the hydroxide of zinc or copper. A. W. Williamson showed in 1850 that if chlorine be passed through water in which finely divided calcium carbonate is suspended, hypochlorous acid and calcium chloride are formed, and carbon dioxide is given off. The hypochlorous acid can be distilled from the liquid. In the cold when there is not a large excess of calcium carbonate, A. Richardson showed that the reaction can be symbolized : $CaCO_3+2Cl_2+H_2O=CaCl_2+CO_2+2HOCl$. If, however, the amount of carbonate decomposed exceeds one part in 30 parts of water (A. W. Williamson), or if the soln. of hypochlorous acid exceeds 4 per cent. HOCl (A. Richardson), calcium chlorate begins to form—presumably by the reaction : $3HOCl=HClO_3+2HCl$; etc. As the amount of calcium chloride in the soln. increases the ratio of calcium hypochlorite to hypochlorous acid increases. If a soln. of calcium chloride with the calcium carbonate in suspension be heated, calcium chlorate and chloride, oxygen, and free chlorine are formed—here, again, the hypochlorous acid is decomposed into oxygen and chlorine gases. A. W. Williamson also used secondary sodium phosphate. Similar results are obtained by treating aq. soln. of other salts—*e.g.* sodium sulphate, or ferric, zinc, manganese, copper, or lead sulphate—with chlorine gas : $Na_2SO_4+H_2O+Cl_2=NaCl+NaHSO_4+HOCl$.

According to S. Goldschmidt, aq. soln. with 25 per cent. of hypochlorous acid can be prepared by distilling a mixture of chlorine hydrate and yellow mercuric oxide under reduced press. Attempts to prepare the anhydrous acid by distillation in vacuo and condensing the distillate at 0°, −20°, and −80° give the 25 per cent. acid in the first two receivers, and chlorine monoxide in the third vessel. Hence, it is argued that the aq. soln. contains the two balanced systems : $HOCl \rightleftharpoons H^{\cdot}+OCl'$; and $2HOCl \rightleftharpoons Cl_2O+H_2O$. The latter system was investigated by determining the partition coefficient between the aq. soln. and carbon tetrachloride. The equilibrium condition is so much in favour of the hypochlorous acid that an approximately $0.2N$-soln. contains but 0·02 per cent. Cl_2O. The superior oxidizing power of hypochlorites in acid as compared with alkaline soln. is said to be due to the chlorine monoxide contained in the former.

A. J. Balard,[9] in 1821, also prepared **hypobromous acid** in a similar manner, namely, by the gradual addition of mercuric oxide of bromine water, and thoroughly shaking the mixture after each addition. Further, quantities of bromine and mercuric oxide can be added until the yellow fluid contains between 6 and 7 parts of HOBr per 100 c.c. The mercuric oxide can be replaced by silver oxide, silver or mercuric nitrate, mercuric acetate, etc. The soln. with 6–7 parts of HOBr per 100 c.c. decomposes at 30°, but more dil. soln. when distilled under ordinary atm. press. give a distillate of bromine followed by a straw-yellow fraction which is a dil. aq. soln. of hypobromous acid. The decomposition is not so pronounced if it be conducted at 40° under a press. of, say, 50 mm. of mercury.

G. Meillère, and A. Job and J. Clarens prepared a soln. of hypobromite, suitable for estimating urea in urine, by mixing *eau de Javelle* with an aq. soln. of potassium bromide ; and A. Fouchet mixed a soln. of 42 grms. of sodium bromide, and 8·5 grms. of sodium chlorate made to 100 c.c. with water, with a soln. of 50 c.c. of hydrochloric acid and 50 c.c. of water ; he then heated 30 c.c. of the first solution

temp. A. Schwicker's measurements (1895) of the velocity of the reaction: $3KOI \rightarrow KIO_3 + KI$, show that the reaction is of the second not the third order. According to C. Casanova and L. Carcano, the reaction between iodine and water: $H_2O + I_2 \rightleftharpoons HI + HIO$, cannot be demonstrated because of the reversibility of the reaction, but if the acids are fixed by means of an alkali, the formation of the hypoiodite is readily demonstrated. If a few crystals of iodine be dissolved in 10 per cent. potassium hydroxide soln., and a few drops be added immediately to a soln. of manganese sulphate, a dark brown precipitate of a higher oxide of manganese is formed; whereas if the soln. of iodine in the alkali lye be boiled and then added to the manganese sulphate soln., a white precipitate of manganese hydroxide is formed owing to the hypoiodite having changed to the iodate. Further, if alcohol be added to a cold solution of iodine in potash lye, yellow iodoform is precipitated, but if the iodine solution has been previously warmed, C. M. van Deventer and J. H. van't Hoff find that the brown colour disappears and no iodoform is produced when alcohol is added, presumably because the first-named soln. contains a hypoiodite, and the latter iodide and iodate. J. Bougault showed that the reaction is so rapid with sodium hydroxide that the formation of iodate is almost complete in a few minutes; the reaction is slower if sodium carbonate is used instead of the hydroxide; and with sodium hydrocarbonate no iodate can be detected even after several days, but the presence of hypoiodite can be readily recognized.

According to A. Schwicker (1891), if urea is added to a freshly prepared conc. soln. of iodine in potassium hydroxide, there is a copious evolution of nitrogen, presumably by a reaction analogous with that involved when urea is mixed with an alkali hypobromite. Iodine monochloride gives a brown soln. with water; this does not at first blue starch, though it gives up iodine to benzene; alkaline soln. of iodine monochloride colour starch blue, and redden benzene. Hypoiodous acid is probably formed which then decomposes into iodide and iodate or iodine and hydriodic acid. According to E. Lenssen and J. Löwenthal,[12] the reaction between potassium hydroxide and iodine is reversible: $2KOH + I_2 \rightleftharpoons KI + KOI + H_2O$, for the iodide and hypoiodite so formed react to reproduce iodine and potassium hydroxide, as well as to form potassium iodide and iodate: $3KOI = 2KI + KIO_3$. This explains how C. F. Schönbein found that the colourless liquid obtained by the action of iodine on a soln. of potassium hydroxide even when the latter is in twofold excess—gives a blue colour with starch paste. Like chlorine and bromine, therefore, iodine reacts with alkali hydroxides to form hypoiodites, and F. Förster and K. Gyr prefer the equation: $I_2 + KOH \rightleftharpoons HOI + KI$; the hypoiodous acid is hydrolyzed: $HOI + H_2O \rightleftharpoons HOH + HOI$, very much more than the corresponding hypobromite or hypochlorite. Consequently, unless a considerable excess of the alkali hydroxide is present, the hypoiodite rapidly changes to the iodate: $2HOI + KOI = KIO_3 + 2HI$. With an excess of alkali hydroxide, the hypoiodite can be prepared free from iodate. It is also believed that hypoiodous acid is so weak that it can be ionized: $HIO \rightleftharpoons H^{\cdot} + IO'$, as well as $HIO \rightleftharpoons I^{\cdot} + OH'$, that is, hypoiodous acid is an amphoteric electrolyte. The conditions which favour the formation of iodate are (i) an elevated temp.; (ii) high conc. of iodide; and (iii) low alkalinity of the soln.

Although hypochlorous acid is formed when chlorine monoxide is dissolved in water: $Cl_2O + H_2O = 2HOCl$, this process of preparing the acid is highly inconvenient; and no corresponding monoxide of bromine or iodine is known. Hypochlorous acid may, however, be obtained from its salts by the action of an acid or an acid salt. For instance, J. L. Gay Lussac[13] made a soln. of the acid by gradually adding sufficient 5 per cent. nitric acid to a litre flask containing some bleaching powder, so as to convert about half the lime into calcium nitrate, $Ca(NO_3)_2$: the main products of the reaction are calcium nitrate, calcium chloride, and hypochlorous acid. If much more nitric acid is added, some hydrochloric acid is formed by reaction with the calcium chloride: $CaCl_2 + 2HNO_3 = 2HCl + Ca(NO_3)_2$, and this acid reacts with the hypochlorous acid producing chlorine and water: $HOCl + HCl$

$=Cl_2+H_2O$. To avoid local super-saturation with nitric acid the liquid is constantly agitated during the addition of the nitric acid. The clear liquid is then distilled The hypochlorous acid comes over with the first portion of the distillate. A soln. of *eau de Javelle* may be treated with nitric acid in a similar manner. Instead of using nitric acid, some other mineral acid may be used. R. Lauch recommended boric acid, since a very great excess must be present before any appreciable quantity of hydrochloric acid is liberated.

A. J. Balard and J. Kolb showed that the soln. of alkali hypochlorite or of bleaching powder may also be distilled with the sulphates of magnesium, zinc, aluminium, or other metal which acts as a feeble base. Calcium or alkali sulphate and a hypochlorite of the heavy metal is formed. The latter is so readily hydrolyzed by water that the hypochlorous acid is obtained by distilling the soln. A. W. Williamson showed that *hypochlorous acid is also formed by saturating a soln. of bleaching* powder or baryta water with chlorine gas, passing air through the liquid in order to drive off the free chlorine, and finally distilling the liquid. Carbon dioxide *liberates hypochlorous acid from hypochlorites and hypobromous acid from hypobromites.* W. Dancer made an aq. soln. of hypobromous acid by passing carbon dioxide through a very dil. soln. of a hypobromite and subsequently distilling the soln. Hypochlorous acid can be prepared in a similar manner. P. T. Austen liberated hypochlorous acid from bleaching powder by treating it with sodium bicarbonate. Thus, A. Wohl and H. Schweitzer treated a soln. of 50 grms. of sodium bicarbonate in darkness with chlorine, until a sample of the liquid when warmed with barium chloride no longer gave a precipitate of barium carbonate. The soln. was continually stirred and cooled with ice during the passage of the gas. Solutions of the alkali carbonates also furnish hypochlorous acid when a current of chlorine is passed through them.[14] According to T. Seliwanoff, nitrogen chloride can be regarded as a tertiary amide of hypochlorous acid, and it furnishes this acid when treated with water. T. Seliwanoff [15] also reported the formation of hypoiodous acid along with iodyl succinamide, $C_2H_4:(CO)_2:NI$, by *the action of mercury succinamide on a dry soln. of iodine in acetic* ether; and in the decomposition of iodyl acetamide, $CH_2.CO.NHI$, by an excess of water. The organic nitrogen iodides of F. Raschig—*e.g.* NI_2CH_3; $NI(CH_3)_2$; etc.—are regarded as amides of hypoiodous acid; and the iodides of the aromatic sulphuric acids of R. Otto and J. Troeger—*e.g.* $C_6H_5SO_2I$ are regarded as mixed anhydrides of sulphuric and hypoiodous acids. According to A. Hantzsch, hypoiodites are produced during the hydrolysis of triazoiodide, N_3I. F. D. Chattaway also found hypoiodites are formed in some of the decomposition which nitrogen iodide undergoes. F. Raschig also noted the intermediate formation of hypobromous acid in the reaction between bromine and dimethylamine.

Hypochlorous acid is also formed when a mixture of air and hydrogen chloride is passed through strong oxidizing agents—*e.g.* W. Odling [16] used a mixture of potassium permanganate or magnanese dioxide and sulphuric acid. T. Fairley oxidized chlorine water with hydrogen peroxide: $Cl_2+H_2O_2=2HOCl$, and P. Lebeau oxidized chlorine water with fluorine; $Cl_2+F_2+H_2O=2HF+2HOCl$—ozonized oxygen is usually evolved by the action of the excess of fluorine on the water. P. Lebeau also prepared hypobromous acid by the action of the fluorine and of bromine fluoride on bromine water. And, according to F. Förster and K. Gyr, and A. Skrabel, a mixture of iodic and hypoiodous acids is formed when dil. hydriodic acid is oxidized by chlorine, bromine, ozone, potassium permanganate, hydrogen peroxide, etc.

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§ 3. The Properties of the Hypohalous Acids and their Salts

Hypochlorous, hypobromous, and hypoiodous acids are known only in aq. soln.—the two former soln. are yellow in colour, the last is greenish or brown.

Hypochlorous acid smells of the anhydride; hypoiodous acid smells of saffron *or iodoform when in dil. soln. and of iodine in conc. soln.* The **heat of formation** is $Cl+O+H+aq.=HOCl_{aq.}+29.930$ Cals. according to J. Thomsen, or 31.6 Cals. according to M. Berthelot. J. Thomsen's value for hypobromous acid is 26.080 Cals. The **heat of solution** $Cl_2O+aq.=9.44$ Cals. and the calculated value of $Br_2O+aq.=16.19$ Cals., the heat of formation $Br_{gas}+O+aq.=-6.0$ Cals. The **heat of neutralization,** $NaOH_{aq.}+HOCl_{aq}=9.98$ Cals. and of $NaOH_{aq}+HOBr_{aq.}=9.5$ Cals. M. Berthelot gives for $K_2O_{aq.}+Cl_2O_{aq.}=9.6$ Cals. K. Schäfer found identical **absorption spectra** with the alkali, barium, and ethyl hypochlorites; and for alkali hypobromites. The absorption spectra of hypochlorous and hypobromous acid were also observed. W. Bray and E. L. Connolly found the **degree of hydrolysis** of hypoiodous acid in aq. soln.; and at 25°, K, the equilibrium constant in $I_{2aq.}+H_2O=HIO+H^{\cdot}+I'$, is 3×10^{-13}. For the increase in the free energy of this reaction G. N. Lewis and M. Randall found 17.1 Cals. at 25°; and for $I_{solid}+\frac{1}{2}O_2+\frac{1}{2}H_2=\frac{1}{2}HIO_{aq.}-23.3$ Cals. at 25°; and for the free energy of formation of HBrO in aq. soln. −19.739 Cals.

Conc. hypochlorous acid smells of chlorine monoxide, and has a caustic action on the skin; when heated, it gives off a reddish-yellow gas, while the more dil. acid at 100° *gives only a little gas. Conc. soln. of hypochlorous acid lose much of the acid* on warming. The soln. also decomposes slowly in darkness, more rapidly in **light,** and this the more rapidly the more conc. and warmer the soln. Bubbles of chlorine gas appear in the decomposing soln. and chloric acid, $HClO_3$, is formed; according to A. Popper,[1] in sunlight, traces of perchloric acid, $HClO_4$, are formed. The decomposition is very rapid in sunlight. The rapid decomposition of hypochlorous acid in sunlight renders it probable that the action of light on chlorine water results in the formation of the hypochlorous acid by hydrolysis: $Cl_2+H_2O=HCl+HOCl$, and this is at once decomposed: $2HOCl=2HCl+O_2$, so that the hydrolysis goes to completion, and leaves, as final products, hydrochloric acid, water, and oxygen. W. C. McC. Lewis found that both neutral and aq. soln. of sodium hypochlorite may be photochemically decomposed by the light from a mercury-vapour uviol lamp, the principal products of decomposition being sodium chloride and oxygen. The *reaction cannot be brought about with measurable velocity by means of infra-red* rays, the effective region being that of the visible and ultra-violet. The reaction is *approximately unimolecular,* $NaOCl\rightarrow NaCl+O$, *meaning that this change is slow* while the union of the oxygen atoms is rapid—since, in general, the slowest of a series of consecutive reactions determines the rate of the whole reaction. A soln. of the hypochlorite shows a marked absorption band in the ultra-violet, and the results favour Grotthus' law. L. Spencer further showed that the shorter the wave-length, other things being equal, the more effective the decomposition, that is, the greater the velocity constant. The temp. coeff. of the photo-reaction is small. The bleaching of linen by sodium hypochlorite is accelerated by exposure to the light of a uviol lamp rich in ultra-violet rays.

I. Bhaduri found that the decomposition by **heat** is a bimolecular reaction; at low temp. the main reaction is $2NaOCl\rightarrow 2NaCl+O_2$, and a slight side reaction, $3NaClO=2NaCl+NaClO_3$; at a higher temp., the latter is the main reaction. Soln. containing less than 5 per cent. HOCl can be distilled; the more conc. soln. decompose into chlorine, and chloric acid, $HClO_3$, and oxygen: $3HOCl=HClO_3+2HCl$; followed by the reaction $HCl+HOCl=H_2O+Cl_2$, for hypochlorous acid is decomposed *by acids, and with hydrochloric acid and chlorine of both acids is set free. When warmed, hypochlorous acid not only furnishes chloric acid*—$HClO_3$—*as indicated above, but it is also decomposed with the evolution of oxygen:* $2HOCl=2HCl+O_2$. Fairly conc. soln. of the hypochlorites decompose in a similar manner: $3NaClO=NaClO_3+2NaCl$, and when the system has become highly charged with chlorate, an independent side reaction sets in: $2NaClO=2NaCl+O_2$. The evidence for this rests mainly on the observation due to I. Bhaduri (1896), that the amount of hypochlorite found to be decomposed after 3 hrs. heating at 100°

decreases with increasing concentration until a certain minimum value is reached, when the amount decomposed then increases with increasing concentration as shown in the diagram, Fig. 3. M. Berthelot's value for the heat change is: $3KOCl=KClO_3+2KCl+18$ Cals. F. Giordani has also studied the conditions of the formation and decomposition of sodium hypochlorite.

The velocity of the formation of chlorates, bromates, and iodates respectively from hypochlorous, hypobromous, or hypoiodous acid has been studied by A. Skrabal, E. L. C. Forster, H. Kretzschmar, C. Graebe, W. Bray, etc.[2] F. Förster and P. Dolch found that at 50° the conversion of sodium hypochlorite into chlorate is a reaction of the second order, presumably $2NaOCl=NaClO_2+NaCl$; and this is followed by a bimolecular reaction: $NaOCl+NaClO_2=NaCl+NaClO_3$. The velocity constant of the first reaction is 0·00010 at 25°, and 0·0019 at 50°, while that of the second reaction is 0·0035 at 25°, and 0·050 at 50°. The temp. coeff. of the first reaction is 3·5, and of the second, 2·88.

A. Skrabal has shown that in the case of hypoiodous acid in alkaline soln., probably an *alkali hypotri-iodite*, MI_3O, is formed, which reacts like free iodine; and the velocity of iodate formation is determined by the rate of reaction between the hypotri-iodite and the alkali by which iodide and iodate are formed. The kinetic equation, $dx/dt=k[HIO]^2[I']/[OH']$, based on these assumptions fits the observations of E. L. C. Forster. When the concentration of the iodine is small the reaction is of the second order, but the reaction is sometimes of the first order. The nature of the products are dependent on the velocity of the reaction; the formation of the halogenate is accelerated by the addition of halide, and also of hydroxide. A. Skrabal found that the hypobromite reaction with a constant concentration of hydroxyl ions is of the second order, and he believes that the mechanism is analogous to that with hypoiodites, or that the equilibrium, $HBrO+H^{\cdot}+Br'\rightleftharpoons Br_2+H_2O$, or $2HBrO+Br'+H^{\cdot}\rightleftharpoons HBr_3O+H_2O$, is rapidly established, and the observed velocity is determined by the decomposition of Br_2 or of the *alkali hypotribromite*, MBr_3O, into bromide and bromate. The velocities of formation of the halogenate from the hypohalogenite increases in passing from hypochlorous to hypobromous and to hypoiodous acids in the proportion $1:3\times10^4:3\times10^6$. The velocity constant, k, of the reaction: $3HOCl=HClO_3+2HCl$, $dx/dt=k[HClO]^3$, at 25°, is 0·0023; and for the corresponding reaction with hypobromous acid, $k=0·25$; and with hypoiodous acid k is very large. Still further, hypobromous acid, being weaker than hypochlorous acid, is more hydrolyzed in alkaline soln., and with hypoiodous acid, the hydrolysis is still greater. Consequently, hypoiodous acid is stable only when the soln. are very dil., or in the presence of a very large excess of alkali.

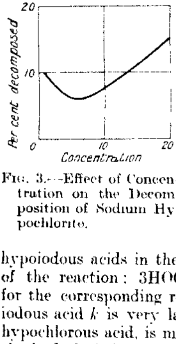

FIG. 3.—Effect of Concentration on the Decomposition of Sodium Hypochlorite.

The decomposition of hypochlorous acid or aq. soln. of the hypochlorites is particularly active in sunlight, and in the presence of oxidizing agents; but soln. of alkali hypochlorites are more stable than the free acid, for they can be boiled without decomposition. Aq. soln. of the hypochlorites decompose slowly with the evolution of oxygen even in darkness—but J. M. Kolthoff kept solutions two months in darkness without appreciable change—the reaction is faster in daylight, and faster still in sunlight. According to I. Bhaduri, the more refrangible the rays, the greater the speed of the decomposition. There appears to be two consecutive reactions: $3NaOCl=NaClO_3+2NaCl$, and $2NaOCl=2NaCl+O_2$. The former prevails in the more conc. soln. of the hypochlorites, the latter in the more dil. soln. According to H. Fonzes-Diacon, the Javelle extracts lose very little of their activity if exposed to light for four months in deep yellow bottles. According to G. E. Cullen and R. S. Hubbard, soln. may be stabilized for use by the addition of 0·5 per cent. of borax, by the addition of 1 per cent. of sodium carbonate; or of

or 2 per cent. of sodium hydroxide. The ready decomposibility of hypochlorous acid and the hypochlorites is connected with the bleaching properties of these agents. Litmus, a soln. of indigo in sulphuric acid, etc., are decolorized. Like *chlorine, and other oxidizing agents, hypochlorous acid colours diphenylamine blue.* According to A. J. Balard, on electrolysis, hypochlorous acid gives no gas at the cathode, and at the anode it gives at first pure oxygen and later a mixture of oxygen and chlorine.

M. de Mallman believes that when soln. of chlorine and sodium hypochlorite are mixed, the reversible reaction can be symbolized: $Cl_2+NaOCl+H_2O \rightleftharpoons 2HOCl+NaCl$. Hypochlorous acid is so feeble in strength that the carbon dioxide of the air is sufficient to displace the acid from hypochlorites forming carbonates, *e.g.* P. T. Austen found a soln. of bleaching powder liberates the free acid when treated with sodium hydrogen carbonate,[3] $NaHCO_3$; and barium carbonate is precipitated from a soln. of barium hypochlorite, and hypochlorous acid remains in soln. With *an aq. soln. of calcium hypochlorite, calcium carbonate is similarly precipitated* chlorine gas is also evolved and some calcium chloride remains in soln.[4] Phosphoric acid behaves similarly. Oxalic acid is oxidized to carbon dioxide, and some chlorine is evolved; sulphurous acid is similarly oxidized to sulphuric acid with very dil. soln. of hydrochloric acid, the free acid is obtained but with more conc. soln., hydrochloric acid is oxidized to chlorine: $NaOCl+2HCl=NaCl+H_2O+Cl_2$; and similarly with dil. and conc. sulphuric acid in the former case, hypochlorous acid is liberated, and in the latter case, remembering that chlorides are usually *present in the same soln.*, $NaOCl+2H_2SO_4+NaCl=2NaHSO_4+H_2O+Cl_2$.

Hypochlorous acid and aq. soln. of the hypochlorites are decomposed by **oxidizing agents:** thus with silver oxide: $Ag_2O+2HOCl=2AgCl+H_2O+O_2$. In 1841, J. L. Gay Lussac [5] found that the addition of powdered pyrolusite augmented the speed of the reaction by which hypochlorous acid or hypochlorites decompose into oxygen, etc., and E. Mitscherlich found an evolution of oxygen even at 4°. T. Fleitmann based a process for the preparation of oxygen by warming hypochlorites with nickel, cobalt, copper, or ferric oxide—lead and bismuth peroxides are inactive. According to R. Böttger, barium peroxide does not decompose the hypochlorite soln., but it gives off half its oxygen. The metals by forming the oxides, act in a similar way, so that the hypochlorites should not be kept in contact with such metals—*e.g.* **copper** and **iron**; **lead** has but a *slight action*; *zinc no appreciable* action. In the preparation of oxygen by T. Fleitmann's process, a little **nickel or cobalt nitrate** soln. is added to water containing hypochlorous acid and the mixture warmed in a flask, oxygen is evolved: $2HOCl=2HCl+O_2$. The cobalt salt acts as a catalytic agent. In illustration, 20 c.c. of soln. of bleaching powder containing the eq. 3·14 grms. of available chlorine at nearly 78° gave off oxygen at the rate of 0·0018 c.c. per minute under conditions where a similar soln. containing a little cobalt nitrate eq. to 0·00047 grm. of cobalt gave off 0·10 c.c. of oxygen per minute. *Consequently, the presence of the catalytic agent favours the reaction:* $2NaOCl=O_2+2NaCl$, which proceeds without the formation of an appreciable quantity of the chlorate: $3NaOCl=NaClO_3+2NaCl$. The mechanism of the reaction is generally supposed to involve the concurrent reactions corresponding with the transformations of the cobalt oxide, Co_2O_3, and peroxide, Co_4O_7, such that $Co_4O_7+CaOCl_2=CaCl_2+2Co_2O_3+O_2$. The cyclic changes of the cobalt oxide during the catalysis of the reaction are symbolized: $Co_2O_3 \rightarrow Co_4O_7 \rightarrow Co_2O_3 \rightarrow Co_4O_7 \rightarrow$ etc. The reaction proceeds faster in the presence of **acids** and salts with an acid reaction, *and it proceeds more slowly in the presence of alkalies or of salts with an alkaline* reaction. The speed is augmented nearly threefold per 10° rise of temp. The speed of decomposition of the bleaching powder is that of a unimolecular reaction such as is symbolized: $CaOCl_2=CaCl_2+O$.

G. F. Jaubert's *oxolith* is a mixture of bleaching powder with one-third its weight of **sodium peroxide** compressed in the form of briquettes, which gives off oxygen in contact with water: $Ca(OCl)Cl+Na_2O_2+H_2O=2NaCl+Ca(OH)_2+O_2$. When oxygen

is prepared by this process, bleaching powder suspended in water is the usual source of the hypochlorous acid. In illustration of the oxidizing action of hypochlorous acid, in alkaline soln., if calcium hypochlorite or bleaching powder be boiled with a soln. of lead acetate or nitrate in alkaline soln., a white precipitate of lead hydroxide is first deposited, this changes to yellow, orange, and finally puce-coloured lead dioxide, PbO_2. In symbols, $Pb(NO_3)_2+2NaOH+NaOCl=PbO_2+2NaNO_3+NaCl+H_2O$. If basic lead acetate is used, there is no need to add the alkali hydroxide; and if boiled in alkaline soln. with a manganous salt, manganese dioxide, MnO_2, or hydrated dioxide, $MnO(OH)_2$, will be precipitated: $MnCl_2+NaOCl+2NaOH=MnO(OH)_2+3NaCl$. More prolonged boiling may give a green soln. of calcium manganate, or a pink coloured soln. of calcium permanganate, $Ca(MnO_4)_2$. According to T. Fairley,[6] when **ozonized air** is passed through a soln. of hypochlorous acid or a hypochlorite, perchloric acid, $HClO_4$, or a perchlorate is formed; and, according to C. F. Schönbein, **hydrogen peroxide** reduces the hypochlorites, giving off a volume of oxygen eq. to twice that contained in the hypochlorite: $KOCl+H_2O_2=KCl+H_2O+O_2$, and on this G. Lunge has founded a method of evaluating hypochlorites from the volume of oxygen obtained when the sample is treated with an excess of hydrogen peroxide. When treated with **sulphur**, hypochlorous acid, or hypochlorites, furnish sulphur chloride, chlorine, and sulphuric acid; **sulphur dioxide** gives sulphuric acid and chlorine; **hydrogen sulphide** (not in excess) gives sulphuric acid and free chlorine; and **carbon disulphide** gives carbon dioxide, sulphuric and hydrochloric acids, and, according to J. O. Ritsema,[7] with hypochlorites in alkaline soln.: $8KOCl+CS_2+6KOH=2K_2SO_4+K_2CO_3+8KCl+3H_2O$. F. Diénert and F. Wandenbulcke find that in dil. soln. **sodium thiosulphate** and hypochlorite react $2Na_2S_2O_3+5Cl_2+5H_2O=Na_2SO_4+8HCl+H_2SO_4+Na_2S_4O_6+2NaCl$; or $5NaOCl+3Na_2S_2O_3+5H_2O=2Na_2SO_4+Na_2S_4O_6+5NaCl+5H_2O$; but in the presence of acids, or even sodium hydrocarbonate, less thiosulphate is used: $Na_2S_2O_3+4Cl_2+5H_2O=2NaHSO_4+8HCl$. **Selenium** is oxidized, forming selenic and selenious acids, and chlorine. Hypochlorous acid is not decomposed by **carbon** or **carbon dioxide**; **nitric oxide** is oxidized to nitric acid; **phosphorus** or **phosphine** gives phosphorous and hydrochloric acids, and a little chlorine; the **phosphorous acids** are oxidized to phosphoric acids; and **phosphorus sulphide** gives *sulphuric, phosphoric, and hydrochloric acids and a little chlorine.* **Arsenic** inflames with hypochlorous acid, forming arsenic acid and arsenic trichloride. The **arsenites** are oxidized to arsenates: $K_3AsO_3+NaOCl=K_3AsO_4+NaCl$, and in J. H. A. Penot's process[8] for estimating hypochlorites in terms of the available or active chlorine, a standard soln. of alkali arsenate is added to the given soln. until a drop of the liquid no longer colours starch and potassium iodide paper blue. This shows that no more available chlorine is present. J. L. Gay Lussac has previously used arsenious acid, As_2O_3, for the same purpose, but the use of the alkali salt prevents the escape of chlorine and is a safer process. J. H. A. Penot's method is also used for bleaching powder whose commercial value depends on the proportion of available chlorine it contains. The amount of sodium arsenite used in the experiment is related with the bleaching powder by the following equation: $Ca(OCl)Cl+Na_3AsO_3=Na_3AsO_4+CaCl_2$, and the theoretical amount of $Ca(OCl)OCl$ can therefore be readily computed.

Example.—20 grms. of bleaching powder were made up with water to a litre, and 25 c.c. were titrated with $\frac{1}{10}N$-standard sodium arsenite soln., *i.e.* a soln. of such a concentration that 1 c.c. corresponded with 0·00355 grm. of chlorine. After the addition of 46 c.c. of the standard soln., a drop of the liquid being titrated gives no coloration with starch and potassium iodide. Here $46\times0·00355=0·163$ grm. of available chlorine was contained in 25 c.c. of the given soln.; or 6·5 grms. per litre of the soln., *i.e.* in 20 grms. of the sample. Hence the sample contained 32·5 per cent. of available chlorine.

G. Blattner studied the action of **metallic oxides** on the alkali hypochlorites and on bleach liquor during 15–20 days. The oxides of cobalt, nickel, and copper

reduced the available chlorine of bleaching powder to chloride in 3 days; ferric oxide acted more slowly; lead and manganese oxides act very slowly; zinc oxide has no appreciable action. Similar results were obtained with *eau de Labarraque*. *He also found that the stability of sodium hypochlorite soln. did not increase with* alkalinity, concentration is alone of importance in this respect. Dry metallic oxides act more slowly than the freshly precipitated moist oxides. The **metals** act like the oxides. **Copper** is very injurious to bleach liquors, **iron** next, **lead** is but slightly affected, and **zinc** not at all. B. W. Gerland found that bleach-liquor prepared by Deacon's process contains copper, and it also decomposes above 40°, much more rapidly than the bleach-liquor of Weldon's process which is free from copper. The liquor also decomposes quickly in copper vessels. According to A. D. White, hypochlorous acid [9] slowly attacks strips of **tin,** copper, **nickel**, and **cobalt**, giving off chlorine mixed with more or less oxygen; with **magnesium,** hydrogen alone is obtained; with iron and **aluminium**, a mixture of hydrogen and chlorine is formed. Iron is rapidly oxidized to ferric oxide, tin and copper form oxychlorides. H. P. Pearson found lead is acted upon almost as quickly as lead oxide, forming a brown lead dioxide. The evolution of hydrogen from magnesium and aluminium form so powerful an oxidizing agent as hypochlorous acid is noteworthy. When an excess of **mercury** is shaken with an aq. soln. of hypochlorous acid, a brownish-yellow precipitate of mercuric oxychloride, $HgO.HgCl_2$, is formed; this is decomposed by dil. hydrochloric acid, and mercuric chloride passes into soln. With chlorine water, mercury gives a white precipitate of mercurous chloride, HgCl, insoluble in dil. hydrochloric acid. Hence, the reaction can be used to distinguish between and even to determine quantitatively hypochlorous acid in the presence of free chlorine in soln., and it forms the so-called *W. Wolters' test.*[10] Both chlorine *water and hypochlorous acid form a precipitate when the soln. is shaken up with* mercury until a drop of the liquid no longer colours starch and potassium iodide paper blue. The precipitate can be filtered off, washed, and treated with a slight excess of dil. hydrochloric acid. The mercuric chloride which passes into soln. can be detected by hydrogen sulphide, and its presence indicates hypochlorous acid; the insoluble mercurous chloride represents the free chlorine. The mercurous chloride can be decomposed by boiling it with a soln. of sodium hydroxide. The filtrate when acidified with nitric acid and treated with silver nitrate soln., gives a precipitate of silver chloride. Hypochlorites behave differently from the free acid in that with mercury they form mercuric oxide and a soluble chloride: $Hg+NaOCl=HgO+NaCl$. The hypochlorites have no action on **gold** or **platinum; silver** is slowly converted into the chloride, and, according to L. Soubeiran, a trace of silver oxide is simultaneously formed if finely divided silver is used; but, according to A. J. Balard, **silver oxide** decomposes the hypochlorites with the evolution of oxygen as indicated above.

The metal **sulphides** are converted into sulphates: $CaS+4Ca(OCl)Cl=CaSO_4+4CaCl_2$; **thiosulphates** are oxidized to sulphates; $Na_2S_2O_3+4NaOCl+H_2O=2NaHSO_4+4NaCl$, and the lower oxides or salts of the metals are oxidized, *e.g.* ferrous salts are oxidized to ferric salts: $2FeSO_4+HClO+H_2SO_4=Fe_2(SO_4)_3+HCl+H_2O$, so that by adding a known amount of ferrous salt to the given soln., the excess which remains unoxidized can be determined by titration with a standard soln. of potassium permanganate, or bichromate. The hypochlorites are *transformed into chlorides by reducing agents—e.g. zinc* and sulphuric acids. **Iodine** and the **iodine chlorides** form iodic acid and free chlorine, **hydriodic acid** is oxidized to iodic acid; **bromine** forms bromic acid and free bromine; **hydrobromic acid** is oxidized to bromic acid. **Hydrochloric acid** and hypochlorous acid, below 2° or 3°, form chlorine hydrate. Aq. **ammonia** and hypochlorous acid give nitrogen chloride, free nitrogen, and chlorine.

According to A. J. Balard, hypochlorous acid produces some chloric acid with the **alkali chlorides ;** F. Förster and F. Jorre say that hypochlorous acid and alkali chloride form alkali chlorate: $3HOCl+NaCl=NaClO_3+3HCl$, and free

chlorine: $HOCl+HCl=H_2O+Cl_2$. According to F. von Tiesenholt, there is a reversible reaction: $NaCl+HOCl \rightleftharpoons NaOH+Cl_2$, and with 2 or 3 grms. of anhydrous calcium chloride dissolved in the smallest possible quantity of hypochlorous acid, *there is an energetic development of chlorine, and a formation of calcium hydroxide; some chlorate is formed at the same time. According to J. L. Gay Lussac, hypochlorous acid at about 100°* attacks **metal chlorides** with the evolution of chlorine and oxygen, and the formation of chlorates: according to A. W. Williamson and J. Kolb, the metal chlorides are not attacked in the cold, and on warming the chlorates are formed. Hypochlorous acid precipitates the higher oxides from the chlorides of manganese, tin, lead, iron, cobalt, and nickel; and copper oxychloride from cupric chloride. **Silver chloride** decomposes the acid catalytically.

According to E. and B. Klimenko,[11] each mol. of hypochlorous acid in the presence of **potassium iodide** and hydrochloric acid furnishes two gram-atoms of free iodine; without the hydrochloric acid, one gram-atom of iodine; and, according to T. Seliwanoff, the alkali iodide furnishes the alkali hydroxide and iodine, and there is a reversible reaction between the iodine and alkali hydroxide. G. Lunge and H. Schäppi represent the reaction by the equation: $HOCl+2KI=KCl+I_2+KOH$; accompanied by the slow reversible change: $6KOH+3I_2=5KI+KIO_3+3H_2O$; in the presence of hydrochloric acid, they represent the reaction: $2KI+HOCl+HCl=2KCl+I_2+H_2O$; and in the presence of chlorine: $2KI+Cl_2+HCl=2KCl+I_2+HCl$, without a change in the acidity of the soln. Consequently, by adding a definite quantity of N-HCl and potassium iodide, and titrating the separated iodine with $\frac{1}{10}N$-$Na_2S_2O_3$, and the excess of acid with baryta soln., it is possible to determine hypochlorous acid and chlorine in the presence of one another. According to A. J. Balard, mercurous nitrate, $HgNO_3$, is rapidly transformed into insoluble red oxychloride, and the supernatant liquid rapidly loses its bleaching qualities and forms mercuric chloride. **Silver nitrate** soln. appears to form silver hypochlorite, $NaOCl+AgNO_3=AgOCl+NaNO_3$; and this is immediately converted into a mixture of insoluble silver chloride and soluble silver chlorate: $3AgOCl=AgClO_3+2AgCl$. As a result, one-third of the total chlorine is precipitated as silver chloride.

Hypochlorous acid decomposes **oxalic acid, cyanogen, cyanides, paper,** and many other organic compounds. It reacts with the double ethylene bond, *e.g.* **ethylene**, $CH_2:CH_2$, forming glycol monochlorhydrin, $CH_2OH.CH_2Cl$. Hypochlorous acid and the hypochlorites are regarded as important chlorinating agents in organic chemistry. J. von Liebig,[12] for example, showed that it converted **ethyl alcohol** or **acetone** into chloroform, $CHCl_3$. It does not do so with methyl alcohol. The **carbinol group** is oxidized to formic acid: $4C_2H_5OH+16Ca(OCl)Cl=13CaCl_2+3(HCOO)_2Ca+8H_2O+2CHCl_3$. V. Cofman found that hypoiodous acid gives stable iodo-compounds almost instantly when treated with a **phenol;** neither free iodine nor any other iodine compound acts in this way, and he uses it as a means of volumetrically determining the amount of this acid.

The reactions of the hypobromites are closely analogous with those of the hypochlorites, both in their mode of formation and in other reactions. The hypoiodites also are similar, but they are extremely unstable, rapidly decomposing on warming into iodides and iodates. For example, hypobromous acid decomposes above 60° into bromine and hydrobromic acid, and if silver nitrate is present, silver bromate, $AgBrO_3$, crystallizes out. With silver oxide, Ag_2O, oxygen is developed, the solution becomes colourless, and silver bromide, AgBr, is precipitated. The hypochlorites or hypobromites serve as oxidizing agents for urea and ammonium salts. The latter are decomposed by a reaction symbolized by: $2NH_4Cl+3NaOBr=3NaBr+2HCl+2H_2O+N_2$. The volume of the nitrogen so obtained serves as a measure of the amount of ammonium chloride in the soln.; when bleaching powder is boiled with ammonia or an ammonium salt, a similar reaction occurs: $2NH_3+3Ca(OCl)Cl=3H_2O+3CaCl_2+N_2$.[13] Hypoiodous acid rapidly decomposes into iodine and iodic acid; the decomposition is accelerated by the addition of iodides, by decreasing the concentration of acids in the soln., and by reducing

agents. When warmed with silver nitrate the iodide and iodate are formed. Hypoiodous acid in presence of an excess of alkali, bleaches indigo soln. more strongly than chlorine or hypochlorous acid. Free hypochlorous acid[14] is a comparatively feeble oxidizing agent in comparison with its salts, for the indigo is bleached only after it has been in contact with the free acid for a long time, but it is bleached immediately when a little alkali has been added to the acid. Soln. of hypoiodous acid to which a little free alkali has been added give a brownish-black precipitate with cobalt salts, a brown precipitate with manganous salts, a buff-coloured precipitate with silver nitrate.

Constitution.—Hypochlorous acid, HOCl, is a very weak acid despite the presence of the non-metal chlorine, which gives to hydrochloric acid, HCl, such powerful acidic properties. D. Vorlander,[15] therefore, assumed that the constitution is not H.Cl : O, since such an acid would have a strength comparable with that of hydrochloric acid ; he considers that the chlorine of hypochlorous acid is polyvalent and unsaturated, and accordingly writes the formula HO.Cl. This, says he, is in accord with (i) its feeble acidic properties ; (ii) its ready oxidizibility to chloric acid ; and (iii) the ease with which it is decomposed—particularly into Cl and OH. The relation between water, hypochlorous acid, and chlorine monoxide is graphically shown by the formula :

$$\begin{matrix} {H \atop H}\!>\!O & \qquad {H \atop Cl}\!>\!O & \qquad {Cl \atop Cl}\!>\!O \\ \text{Water.} & \qquad \text{Hypochlorous acid.} & \qquad \text{Chlorine monoxide.} \end{matrix}$$

J. Stieglitz has pointed out that in A. A. Jakowkin's reaction: $Cl_2+H_2O \rightleftharpoons HOCl + H^{\cdot}+Cl'$, part of the hypochlorous acid must form positive chlorine and negative chlorine ions in order to produce the neutral molecules Cl_2 and H_2O. The ionization of hypochlorous acid—as an acid—will be $HOCl \rightleftharpoons H^{\cdot}+OCl'$; and as a base, $HOCl \rightleftharpoons HO'+Cl^{\cdot}$. There is also evidence that not only can hypochlorous act as a weak acid, but it can also act as a weak base. The basic properties of hypochlorous acid are illustrated by the iodoso- and iodonium compounds.[16]

E. J. Müller argues that *the alkali hypochlorites are mixed salts of the formula* M_2OCl_2, or MOCl.MCl, from (i) the similarity of the reactions between calcium hypochlorite, $CaOCl_2$, and the alkali hypochlorites ; (ii) the decomposition of calcium hypochlorite by sodium carbonate : $CaOCl_2+Na_2CO_3=CaCO_3+Na_2OCl_2$; and (iii) the action of sulphuric acid on hypochlorite is more of the character : $Na_2OCl_2+H_2SO_4=Na_2SO_4+Cl_2+H_2O$, than is the case on the assumption that sodium hypochlorite is constituted Na.O.Cl. K. Schäfer prefers the formula $Na<{O \atop Cl}$.

Uses.—The hypochlorites and bleaching powder are used extensively for bleaching cotton, linen, paper, pulp, etc. They are used as disinfecting agents—sewage, purification of water, etc. A soln. with 10 per cent. of available chlorine is said to be as effective as phenol. Soln. of hypochlorites—with their alkalinity neutralized with boric acid—have been used successfully in treating wounds. Hypochlorites are also used as oxidizing and chlorinating agents in organic chemistry.[17]

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§ 4. Bleaching Powder

Bleaching powder has been the subject of numberless researches made with the object of arriving at its constitution, and it may be said that in spite of all these efforts, there is no other substance of equally simple composition regarding whose nature and composition so much doubt prevails.—E. von Meyer (1889).

In 1815, L. G. Gilbert [1] noticed that thoroughly dried calcium oxide or hydroxide does not react chemically with dry chlorine, and similarly, in 1879, J. K. Weisberg showed that the same remark applies to dry barium or strontium oxide. The case is very different if moisture be present. With barium hydroxide two gram-atoms of chlorine are absorbed per gram-atom of the bivalent barium, and barium chloride and chlorate are produced so that if barium hypochlorite is formed as the first product of the reaction, it is immediately decomposed: $3Ba(OCl)_2 = Ba(ClO_3)_2 + 2BaCl_2$; with calcium and strontium hydroxides, the reaction appears to be much

more complex, and probably also with barium hydroxide under conditions where the hypochlorite is not immediately decomposed.[2] The powder obtained by the action of chlorine on moistened slaked lime is called *bleaching powder, chloride of lime, chlorinated lime, chlorure de chaux, Chlorkalk, Bleichkalk, Bleichpulver*, etc. While quicklime absorbs very little chlorine, J. J. Welter, A. Morin, and J. Dalton[3] showed that lime slaked with about half a mol. of water per mol. of lime absorbs about 32 per cent. of chlorine, and much more if more water is present. By carefully regulating the amount of water, G. Lunge and H. Schäppi (1880) prepared a sample of bleaching powder with 43·4 per cent., and H. Ditz, one with 48·74 per cent. of active chlorine. In the latter case, a little water was added to the chlorinated lime and the product again exposed to the action of the chlorine. These operations were repeated a number of times until the lime was saturated. G. Lunge[4] gives the following analysis of a good sample of bleaching powder:

Ultimate Analysis.		Calculated Promixate Composition.	
Lime, CaO	39·89	$2CaOCl_2.H_2O$	82·65
Available chlorine	43·13	$CaCO_3$	0·95
Chlorine as chloride	0·29	$CaCl_2$	0·44
Water, H_2O	17·00	$Ca(OH)_2$	6·80
Carbon dioxide	0·42	H_2O	9·16

with but a trace of chlorine as calcium chlorate. According to A. G. Labarraque,[5] the rate of absorption of chlorine is hastened if the calcium hydroxide is mixed with about 5 per cent. of sodium, potassium, or barium chlorides or sulphates. The absorption of chlorine is accompanied by a rise of temp.; by rapidly saturating lime with chlorine, A. Morin found the temp. rose to 119°, and most of the hypochlorite was converted into chlorate and chloride.

The manufacture of bleaching powder.—Bleaching powder is made on a large scale by the action of chlorine on slaked lime, $Ca(OH)_2$. The lime is as pure as possible, and, after being sieved, is spread in 3- or 4-inch layers on perforated shelves in a large chamber, and then raked into furrows. Chlorine is led through the chambers. At first the absorption of chlorine is rapid, but it afterwards slows down. The lime is then turned over from time to time so as to expose fresh surfaces. After standing for 12 to 24 hours a shower of fine dust lime is blown into the chamber to absorb the excess of chlorine. The chlorine used should be cool and dry, and as free as possible from hydrogen chloride and carbon dioxide. Since the *proportion of moisture* in the system largely determines the percentage amount of available chlorine in the product, it is simplest to work with dry chlorine, and use lime with about 28 per cent. of moisture. G. Lunge and H. Schäppi[6] found that dry chlorine with lime containing different proportions of moisture gave bleaching powders with different amounts of available chlorine:

Moisture in lime	6·5	13·6	24·0	27·8	28·2	31·8 per cent.
Available chlorine	9·1	32·3	40·7	43·4	40·4	36·8 ,,

Hence the proportion of available chlorine increases as the proportion of water increases, and reaches a maximum when the lime contains 27·8 per cent. of water; any further increase in the proportion of water lessens the proportion of available chlorine. The *temperature* of the lime in the chambers is kept between 30° and 40°, since the amount of active chlorine in the product is reduced if the temp. is above or below these limits. For example:

Temp.	−17°	0°	21°	30°	40°	45°	60°	90°
Active chlorine	2·3	19·9	35·5	40·1	41·2	40·5	39·4	4·3

The process just described refers to the conc. chlorine of Weldon's or the electrolytic process; for the more dil. chlorine of Deacon's process, the gas acts less energetically, and the lime is mechanically carried in a direction opposite to the stream of gas, so that the bleaching powder comes in contact with the fresh gas entering the chamber, and the gas which is almost exhausted comes in contact with fresh lime. The product is satisfactory if it contains between 37 and 39 per cent. of available chlorine. The yield of bleaching powder is about 1½ times the weight of lime used. The powder is packed for storage and transport in hard wooden casks or mild steel drums, with lids not hermetically sealed, so as to prevent the vessels bursting explosively should the bleaching powder slowly decompose with the evolution of oxygen: $2Ca(OCl)Cl = 2CaCl_2 + O_2$.

The properties of bleaching powder.—A great many of the properties of bleaching powder, and particularly of the aq. soln., run parallel with those of typical hypochlorites. Bleaching powder is a white pulverulent mass which on exposure to air attracts moisture and carbon dioxide, and forms a pasty mass. It has a peculiar smell, unlike that of chlorine; the smell, says C. A. Winkler,[7] cannot be due to hypochlorous acid, because it is present after boiling soln. with an excess of alkali, and cooling in an atm. free from carbon dioxide; but P. T. Austen has shown that alkaline soln. may contain the free acid. Bleaching powder slowly decomposes even in the absence of air, as is evident by the explosions which have been reported of bleaching powder confined in closed vessels.[8] The decomposition is faster if the powder be exposed to air, heat, and light. The powder does not keep so long in warehouses in India as it does in Europe, and the loss is greater in the summer than in the winter months. The shaking which occurs during transport also makes the powder decompose more quickly than if it is lying quietly in a dark dry place; and consequently, the strength of the powder in available chlorine is guaranteed only at the port of shipment. J. Pattinson[9] has examined the loss which occurs on storage, and found the active chlorine decreased from about 5 to 10 per cent. during a year's storage. According to C. Opl,[10] if bleaching powder is mixed with an equal weight of dried calcium chloride, it loses up to 60 per cent. of its available chlorine if kept two days in darkness. L. M. Bullier and L. Maquenne made an intimate mixture of 60 parts of the bleaching powder with 40 parts of Glauber's salt, and the resulting mixture of sodium hypochlorite and calcium sulphate was found to be very stable.

According to G. Lunge and H. Schäppi,[11] moist air at 80° deprives bleaching powder of much of its oxygen, but not of chlorine—calcium chloride and chlorate are formed; air also deprives the powder of oxygen. Air free from carbon dioxide sweeps out a little hypochlorous acid from a soln. of bleaching powder; this acid is derived from the hydrolysis of the hypochlorite; ordinary moist air (containing carbon dioxide) first liberates from solid bleaching powder a mixture of chlorine and hypochlorous acid, and afterwards chlorine. In aq. soln. the action is similar. The carbon dioxide in the air unites with free lime, and the calcium chloride which is present reverses the action liberating chlorine, for bleaching powder reacts with sodium bicarbonate: $2Ca(OCl)Cl + NaHCO_3 = CaCO_3 + CaCl_2 + NaOCl + HOCl$; and $NaOCl + NaHCO_3 = Na_2CO_3 + HOCl$. Hence, if this be correct, there is free mineral acid present in an alkaline soln. If this soln. be boiled, the hypochlorous acid decomposes into hydrogen chloride and oxygen, and the former decomposes the sodium carbonate so that the escaping gases are oxygen and carbon dioxide; sodium hypochlorite under similar conditions gives no oxygen. If the sodium hypochlorite be treated with carbon dioxide, boiling the soln. then furnishes oxygen gas. Most of the water can be expelled from bleaching powder at 150°: a small proportion is lost at a red heat. H. Ditz made a bleaching powder, $CaO.Ca(OCl)Cl.2H_2O$, which lost a mol. of water in a desiccator over sulphuric acid or in a current of dry air—free from carbon dioxide—at 100°; when further heated to 150°–180°, it lost oxygen, and at a strong red heat, it lost the other mol. of water. According to C. Opl, bleaching powder yields chlorine: $Ca(OCl)Cl = CaO + Cl_2$, when heated in the absence of moisture, and if moisture is present, oxygen is evolved: $2Ca(OCl)Cl = 2CaCl_2 + O_2$, always with the simultaneous formation of chlorate: $6Ca(OCl)Cl = Ca(ClO_3)_2 + Ca_5Cl_{10}$. He could not distinguish between the action of light and heat. An aq. soln. of bleaching powder in sunlight gives a gas containing about 95 per cent. of oxygen. The speed of decomposition in light and the amount of oxygen evolved is proportional to the intensity of the light.[12] According to A. Bobierre, bleaching powder loses its water and becomes pasty when heated to redness, forming calcium chloride and chlorate; at a red heat H. St. C. Deville and H. Debray obtained 50 litres of oxygen from a kilogram of the powder.

If the bleaching powder or the filtered soln. be treated with very dil. nitric, hydrochloric, or sulphuric acid, just sufficient to neutralize the free and combined

lime, hypochlorous acid, HOCl, is formed: $Ca(OCl)Cl+HCl=CaCl_2+HOCl$, and the soln. smells of hypochlorous acid but not of chlorine. The hypochlorous acid can be separated by distillation. If an excess of acid be present, the hypochlorous acid is decomposed, forming water and chlorine: $HOCl+HCl=H_2O+Cl_2$. Dry carbon dioxide has little or no action on dry bleaching powder, but with moist carbon dioxide at 70°, most of the chlorine is removed, although this gas has no action on calcium chloride. According to R. L. Taylor,[13] the action of carbon dioxide on bleaching powder—solid or soln.—is like that of any other acid, for hypochlorous and hydrochloric acids are produced and these decompose one another with the evolution of chlorine.

W. Odling[14] found that alcohol does not extract appreciable amounts of calcium chloride from bleaching powder. When bleaching powder is dissolved in water, it forms a strongly alkaline soln., and an *insoluble residue* is obtained, consisting almost wholly of calcium hydroxide, but it was not possible to remove the last traces of the available chlorine by washing. J. F. Persoz[15] stated that the insoluble residue contains a special bleaching compound which acts more destructively on vegetable fibre than does a soln. of bleaching powder, but, according to G. Lunge, Persoz's statement is wrong; the damage is caused by the fine particles of the powder settling on the vegetable fibre and locally forming conc. soln., which transform cellulose into oxycellulose. The *solution* contains calcium hypochlorite, $Ca(OCl)_2$, the chloride, $CaCl_2$, and the hydroxide, $Ca(OH)_2$,—the amount of the latter corresponds with its solubility. G. Lunge's analysis[16] of a soln. prepared from a good sample of commercial bleaching powder is equivalent to

	$Ca(OCl)_2$	$CaCl_2$	$Ca(ClO_3)_2$	$Ca(OH)_2$
Grms. per litre . .	129·00	10·54	0·38	4·21

G. Lunge also gives a table of specific gravities of soln. of this sample of bleaching powder for different amounts of available chlorine in grams per litre:

Sp. gr. . .	1·0025	1·01	1·02	1·04	1·06	1·08	1·10	1·11
Grms. Cl . .	1·40	5·58	11·41	23·75	35·81	49·06	61·50	68·00

Bleaching powder which has been kept some time will contain more chloride and chlorate. The titre of available chlorine did not change appreciably when kept for 24 days out of contact with air and in the dark, but a slight change was noticeable in 33 days. There was no appreciable loss after keeping 12 days open to air and in darkness, but a loss of about one-eighth of its strength in 33 days. Diffused daylight accelerates the decomposition of the solutions. The pink colour of the soln., obtained by leading carbon dioxide through a warm soln. of bleaching powder or other hypochlorite, has been attributed to manganese—as permanganate—and to iron—probably as calcium ferrate. G. E. Davis[17] established the presence of manganese spectroscopically; and T. L. Bailey and P. H. Jones obtained no pink coloration with soln. free from manganese even when considerable amounts of iron were present.

Whatever be the constitution of bleaching powder it is fairly certain that the aq. extract contains the three compounds hydroxide, chloride, and hypochlorite in soln. The existence of the hypochlorite is evidenced by the isolation of crystals of this salt by C. T. Kingzett. L. T. O'Shea also argued that if the soln. contains a chlorohypochlorite, Ca(OCl)Cl, it will diffuse so that the ratio of the total chlorine to oxidizing chlorine will remain 2 : 1 both in the diffusate, and in the original soln., whereas if the soln. contains the two salts—hypochlorite and chloride—the one will diffuse faster than the other, and the ratio in question will not be the same in the diffusate and in the original soln. It was found that the diffused liquid was richer in chloride and poorer in oxidizing chlorine than in the original soln., showing that the chloride diffused faster than the hypochlorite, and that if solid bleaching powder is a compound of calcium hypochlorite and chloride, or of calcium chlorohypochlorite, it is decomposed by the action of water into a mixture of the two salts. In addition,

M. Duyk has shown that the hypochlorites are hydrolyzed in aq. soln.: $Ca(OCl)_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + 2HOCl$, so that a soln. of bleaching powder with 0·02162 grm. of active chlorine in 10 c.c. contained the eq. of 0·002485 grm. of free hypochlorous acid and 0·0110 grm. of free lime; on adding 100 c.c. of water the free hypochlorous acid and lime were increased to 0·008697 grm. and 0·0137 grm. respectively; and a further addition of another 100 c.c., to 0·01629 grm. and 0·0140 grm. respectively. The hydrolysis is further confirmed by the removal of some of the hypochlorous acid by the passage of a current of purified air through the liquid. F. Förster and H. Bischoff, and A. Sieverts, also attribute the relatively higher bleaching action of soln. of the alkali bleaching liquors prepared electrolytically to the relatively large proportion of free hypochlorous acid they contain.

According to K. Thümmel,[18] a mixture of equal parts of bleaching powder and charcoal explodes when heated in a closed vessel, and, according to H. G. de Claubry, sulphur in place of charcoal acts in the same way. T. L. Phipson found that when exposed to hydrogen sulphide, the latter loses its smell, the odour of chlorine appears, and sulphur is formed. Hypochlorous acid is probably set free, and this reacts with hydrogen sulphide, forming sulphur and chlorine.

Bleaching.—In bleaching by *eau de Javelle* or by bleaching powder, the preliminary treatment is often complex and is determined by the character of the material. Various fatty or colouring agents may have to be extracted by washing in hot alkali lye. The washed fabric is steeped in a clear dil. aq. soln. of the bleaching agent—*chemicking*—and then *soured* by steeping in dil. acid. Hypochlorous acid is thus produced, and then free chlorine. The free chlorine does its work within the fibres of the wet fabric. In high-class goods required to be "brilliant white," the operations may have to be repeated a number of times. The bleaching action of hypochlorous acid is generally stated to be twice as great as that of the chlorine it contains, supposing the latter were free: $2Cl_2 + 2H_2O = 4HCl + O_2$; $4HOCl = 4HCl + 2O_2$; but it must be remembered that two atoms of chlorine are needed to form one molecule of HOCl, since an eq. amount of HCl is formed at the same time.

The constitution of bleaching powder.—In the early days, C. L. Berthollet,[19] J. L. Gay Lussac, and J. J. Berzelius assumed that the powder prepared by C. Tennant in 1798 by the action of chlorine on slaked lime is a compound of lime, CaO, with chlorine, *viz.* $CaOCl_2$; but after his investigation of the hypochlorites in 1835, A. J. Balard[20] concluded that bleaching powder is a compound or a mixture of calcium chloride, $CaCl_2$, and calcium hypochlorite, $Ca(OCl)_2$, mixed with an excess of calcium hydroxide. Numerous attempts have been made to explain the nature of this product, and many contradictory statements have been made about what appear to be questions of fact. Although it is generally agreed that calcium hypochlorite plays an important *rôle*, there is no universal agreement on the constitution of bleaching powder, probably because the attempt has been made to find a constitutional formula for an indefinite mixture, on the assumption that it is a chemical individual. The main discussions can be arranged under the following heads:

(1) *Formulæ based on the assumption that bleaching powder is a mixture of calcium hypochlorite and calcium chloride.*—It will be evident that bleaching powder cannot be the calcium salt of hypochlorous acid, $Ca(OCl)_2$, because the product would then furnish twice the amount of available chlorine actually obtained when it is treated with hydrochloric acid, in virtue of the reactions symbolized: $Ca(OCl)_2 + 4HCl = CaCl_2 + 2H_2O + 2Cl_2$. Hence, A. J. Balard suggested that bleaching powder is a mixture of chloride and hypochlorite, $CaCl_2 + Ca(OCl)_2$. J. L. Gay Lussac confirmed Balard's conclusion that bleaching powder is a mixture of eq. proportions of calcium chloride and hypochlorite. Against this view, it is very probable that *bleaching powder contains but little calcium chloride* because: (1) Nearly all the chlorine can be expelled from bleaching powder by the action of carbon dioxide, but not from calcium chloride. To get over this difficulty, it has been suggested that possibly some reaction like that assumed by A. J. Balard takes place: $CO_2 + Ca(OCl)_2 = CaCO_3 + CaCl_2 + Cl_2O$, followed by $Cl_2O + CO_2 + CaCl_2 = CaCO_3 + 2Cl_2$.

(2) Calcium chloride is very deliquescent, bleaching powder is not. (3) Calcium chloride is readily dissolved by alcohol, whereas an alcoholic soln. of bleaching powder contains but very small quantities of calcium chloride. (4) When bleaching powder is treated with successive small quantities of water, the first washings contain much less calcium chloride than would be the case were calcium chloride present as such in the powder. (5) Bleaching powder made by mixing calcium hypochlorite with sufficient calcium chloride to furnish the same percentage amount of bleaching chlorine as commercial bleaching powder, when treated by moist carbon dioxide gives off an amount of chlorine corresponding with the hypochlorite only, whereas the commercial bleaching powder parts with 80 per cent. of bleaching chlorine. Hence it is inferred that bleaching powder is not a mere mixture of calcium hypochlorite and chloride, but rather a compound of the two, *viz.* Ca(OCl)Cl.

However carefully prepared, *bleaching powder always contains an excess of lime;* at any rate, a deposit of slaked lime is always found as a residue when bleaching powder is extracted with water. Since the available chlorine in commercial bleaching powder usually ranges between 36 and 38 per cent., and under the very best conditions a maximum of about 43·5 per cent. of available chlorine is taken up, it is inferred that the calcium hydroxide, $Ca(OH)_2$, is not completely sat. with chlorine, and that calcium hydroxide is present—either free or combined.

(2) *Formulæ based on the assumption that bleaching powder is a double salt of calcium chloride and hypochlorite.*—As emphasised by K. Kraut,[21] the non-deliquescent character of bleaching powder may of course mean that the calcium chloride and hypochlorite are united to form a double salt, $CaCl_2.Ca(OCl)_2$, which has not quite the same meaning as the simplified formula, Ca(OCl)Cl, but is rather analogous with the non-deliquescent double salt of calcium chloride and acetate, $CaCl_2.(CH_3COO)_2Ca.5H_2O$. Mol. wt. determinations are not available. Attempts to decide between these two formulæ—$CaCl_2.Ca(OCl)_2$ and Ca(OCl)Cl – by the extraction with solvents have not been successful, because the solvent may react with the compound—*e.g.* W. von Tiesenholt noted that when bleaching powder is shaken up with carbon tetrachloride, two powders of different density and with a different proportion of active chlorine are formed; the same thing occurs when alcoholic chloroform reacts with the hypochlorite. Similarly, the fact that carbon dioxide drives most of the chlorine may mean that the hypochlorous acid hydrolytically dissociated or expelled from its salts by carbon dioxide attacks the chlorides yielding chlorine and the free base or a carbonate, $MCl+HOCl=MOH+Cl_2$. F. Förster has obtained direct evidence of the reaction: $NaCl+6HOCl=NaClO_3+3H_2O+3Cl_2$, and W. von Tiesenholt found that a soln. containing equimolecular proportions of calcium hypochlorite and chloride gives off more chlorine than would be furnished by calcium hypochlorite alone. A. Thiel, however, points out that W. von Tiesenholt's conclusion does not follow from his experiments, for they only show that when bleaching powder is dissolved in water, a mixture of the chloride and hypochlorite is formed. W. von Tiesenholt later showed that chlorine is expelled from moist artificial mixtures of the solids at a temp. between 40° and 100°. Hence, the expulsion of chlorine from bleaching powder does not decide in favour of the mixed salt, Ca(OCl)Cl, against the double salt, $CaCl_2.Ca(OCl)_2$. H. Ditz, however, has shown that W. von Tiesenholt's formula does not account for the loss of water which occurs when bleaching powder is heated to 100° in a stream of dry air, free from carbon dioxide, and the loss of oxygen on further heating to 150°–180°.

(3) *Formulæ based on the assumption that bleaching powder is a hydroxyhypochlorite.*—In 1859, P. A. Bolley[22] suggested that the calcium hydroxide of bleaching powder is mixed with it in a mechanical way, and it represents the cores of the granules which escaped chlorination by being encrusted with bleaching powder proper. R. Fresenius and F. Rose suggested that bleaching powder is a hydrated oxychloride and hypochlorite: $Ca(OCl)_2.CaCl_2.2CaO.4H_2O$. This would mean that bleaching powder can contain as a maximum 32 per cent. of available chlorine, although if, as K. Kraut suggested, the basic chloride or oxychloride be $CaCl_2.CaO$,

the theoretical proportion of available chlorine would approximate closer to the observed value, but would still be less than the maximum obtainable. J. Kolb suggested the formula: $2CaOCl_2.H_2O.Ca(OH)_2$, and assumed that the double compound is split by water into insoluble calcium hydroxide, and soluble calcium hypochlorite, but the formula gives a maximum of 38·7 per cent. of available chlorine—less than the observed value. C. Stahlschmidt suggested the formula: $2Ca(HO)(OCl)CaCl_2.2H_2O$. In order to make the assumption fit the facts, it is supposed that the basic calcium hypochlorite, HO.Ca.OCl, invented by C. Stahlschmidt is not attacked by chlorine, and is decomposed by water into calcium hypochlorite and hydroxide: $2Ca(OH)(OCl)=Ca(OCl)_2+Ca(OH)_2$. C. Stahlschmidt's formula: $2Ca(OH)OCl.CaCl_2.2H_2O$, required a maximum of 39 per cent. for the available chlorine—this is less than the observed maximum; the presence of calcium chloride, $CaCl_2$, is an assumption which cannot be granted. In 1884, E. Dreyfus based some arguments for C. Stahlschmidt's formula on some experiments which G. Lunge and R. Schoch showed to be erroneous.

(4) *Formula based on the assumption that bleaching powder is a chloroperoxide.*—In 1803, C. L. Berthollet suggested that the composition of bleaching powder corresponds with the formula $CaOCl_2$, and many chemists have accepted a similar formula, but with different interpretations. For example, N. A. E. Millon [23] regarded bleaching powder as a kind of peroxychloride, O : Ca : Cl_2; C. Göpner, $(CaO)Cl_2$; E. Richters and G. Juncker, W. Wolters, and C. Opl likewise maintain that although bleaching powder and its soln. both contain the compound $CaOCl_2$, this is not a mixture of hypochlorite and chloride. J. Mijers,[24] like N. A. E. Millon, assumes a peroxide formula, and represents the formula by $Cl_2=Ca=(OH)_2$, on the assumption that the calcium atom is quadrivalent. This formula may also be regarded as a monohydrate of W. Odling's Cl—Ca—OCl. N. Tarugi also considers bleaching powder to be a chloride of calcium peroxide, because when dehydrated lime is left exposed to the air, it exhibits a peroxide reaction—colouring tincture of guaiacum blue; ether and chromic acid, blue; and ferrous sulphate and potassium thiocyanate, red. He considers that bleaching powder is therefore $CaO_2Cl_2.H_2O$, corresponding with a maximum of 44·09 per cent. of available chlorine; with its action of mercury on bleaching powder: $CaO_2Cl_2+Hg=CaO_2+HgCl_2$; and with the fact that in order to get the best quality of bleaching powder free oxygen is necessary. H. Ditz, however, contradicts several of N. Tarugi's statements.

(5) *Formula based on the assumption that bleaching powder is a chlorohypochlorite.*—W. Odling [25] suggested that when chlorine is allowed to act upon a bivalent base—say, calcium hydroxide, $Ca(OH)_2$—a molecule of each of the two monobasic acids—hydrochloric and hypochlorous acids—formed by the action of chlorine on water, is neutralized by one molecule of the base, and what seems to be a **mixed salt** is formed:

$$Ca<\begin{matrix}OH\\OH\end{matrix}+\begin{matrix}HOCl\\HCl\end{matrix}=Ca<\begin{matrix}OCl\\Cl\end{matrix}+2H_2O$$

W. Odling, therefore, regarded bleaching powder as a mixed salt—hypochlorite and chloride. Against this view, K. Kraut cited the formation of lithia bleaching powder, but G. Lunge and P. Naef showed that lithia bleaching powder is fundamentally different from lime product.

E. Schwarz found that the bivalent bases baryta and strontia give compounds analogous in properties with that from lime. *Baryta bleaching powder* is very unstable, while *strontia bleaching* powder is more stable and is readily prepared.[26] G. Lunge has further shown that the various properties of bleaching powder are best co-ordinated by assuming that the active agent is the mixed salt formulated Cl.Ca.OCl by W. Odling. This view is further confirmed by L. Limpach, L. T. O'Shea, E. Schwarz, etc. After washing samples of bleaching powder with alcohol to remove calcium chloride, L. T. O'Shea determined the ratios indicated below, and

compared them with the values computed for other formulæ. He found W. Odling's formula alone gave results in accord with observations:

	CaO : Total Cl.	Available Cl. : Total Cl.	CaO : Available Cl.
Observed	1 : 2	1 : 2	1 : 1
Calculated Stahlschmidt—Ca(OH)Cl	1 : 1	1 : 1	1 : 1
,, Gay Lussac—$Ca(OCl)_2$.	1 : 2	1 : 1	1 : 2
,, Odling—Ca(OCl)Cl .	1 : 2	1 : 2	1 : 1

E. Schwarz assumes that the fundamental reaction is: $H_2O+Cl_2 \rightleftharpoons HCl+HOCl$. So long as an excess of free lime is present, the reaction is merely one of neutralization, *but as soon as the lime is used up, the excess of hydrochloric acid liberates* hypochlorous acid from the bleaching powder, and this in conjunction with the hypochlorous acid formed by the action of chlorine on water oxidizes the undecomposed hypochlorite to chlorate. The excess of chloride always found in commercial bleaching powder is mainly derived from the hydrogen chloride present in the chlorine used. If an excess of water is present, the hypochlorite is hydrolyzed. When treated with carbon dioxide synthetic bleaching powder prepared by the action of chlorine monoxide on calcium oxide in the presence of moisture gives up less chlorine than the product obtained by the action of chlorine on slaked lime. This is supposed to be explained by the assumption that the former is a mixture of calcium hypochlorite and chloride, whereas the latter is a mixed salt, CaCl(OCl). H. Ditz[27] considers that commercial bleaching powder is not a homogeneous chemical individual, but rather a mixture formed by a series of reactions, the first of which is represented: $2Ca(OH)_2+Cl_2=H_2O.CaO.Ca(OCl)Cl+H_2O$. If a sufficient excess of water be present, and the temp. be not too low, this product is hydrolyzed: $H_2O+H_2O.CaO.Ca(OCl)Cl=Ca(OH)_2+H_2O.Ca(OCl)Cl$, and the $Ca(OH)_2$ so produced is available for rechlorination. The bleaching powder so formed is a mixture of both $CaO.Ca(OCl)Cl.H_2O$ and $H_2O.Ca(OCl)Cl$. The compound $CaO.Ca(OCl)Cl.H_2O$, or $2Ca(OH)_2.CaCl_2.Ca(OCl)_2$, is formed at $-10°$; and the compound $Ca(OCl)Cl.H_2O$ has also been produced at higher temp. In practice, these reactions are modified by the amount of water in the slaked lime, and they do not usually proceed beyond the stage represented by a final product: $(2n-2)Ca(OCl)Cl+CaO.Ca(OCl)Cl.H_2O+(2n-1)H_2O$. The complex $H_2O.CaO.Ca(OCl)Cl$ appears to be stable at 100°, but is decomposed at 130° with the evolution of oxygen; the molecule of water, however, is not expelled below a red heat. The formation of bleaching powder, says H. Ditz, is not a simple process, but several reactions succeed one another giving different products. Indeed, he was able to make a product with 48·74 per cent. of available chlorine and 0·64 per cent. of non-chlorinated lime, by adding a little water from time to time. According to F. Winteler, the moisture plays the part of a catalytic agent, in the formation of bleaching powder. Chlorine water is first formed; this hydrolyzes: $Cl_2+H_2O \rightleftharpoons HCl+HOCl$—the hydrochloric acid reacts most rapidly with the lime, forming Ca(OH)Cl *and* $CaCl_2$: *some water is formed at the same time.* The hypochlorous acid acts on the original $Ca(OH)_2$, on the Ca(OH)Cl, and on the $CaCl_2$, with the result that the finished product may contain

$$Ca{<}^{OH}_{OH} \qquad Ca{<}^{OH}_{Cl} \qquad Ca{<}^{Cl}_{Cl} \qquad Ca{<}^{OCl}_{OH} \qquad Ca{<}^{OCl}_{OCl}$$

as well as free hypochlorous acid, which then forms chloride and oxygen, or chloride and chlorate. Hence, says F. Winteler, bleaching powder is not a homogeneous product, and no definite constitutional formula can be assigned to it. Otherwise expressed: ***Chlorinated lime is not a homogeneous individual but rather a mixture of calcium chlorohypochlorite, Ca(OCl)Cl, or a double salt, $CaCl_2.Ca(OCl)_2$, with other products, the relative proportions of which depend upon the conditions under which the chlorination has been performed***—temperature, proportion of water present, rate at which the chlorine is led over the lime, etc. It is convenient to assume that bleaching

powder is eq. to Ca(OCl)Cl with more or less free calcium hydroxide. The arguments, however, are not final. As Roger Bacon once said: Argument may appear to decide a question, but it cannot make us feel certain unless the truth be also established by experience.

In 1832, J. J. Berzelius prepared *bromine bleaching powder*, or *bromide of lime*, by the action of bromine on slaked lime. By heating calcium hydroxide suspended in water with iodine, G. Lunge and R. Schock[28] obtained a colourless soln. which bleached vegetable colouring matters—logwood, litmus, and cochineal—gave no coloration with starch; gave a separation of iodine when treated with acids; gave an evolution of oxygen with hydrogen peroxide; decomposed slowly in darkness, rapidly in sunlight; and even on long boiling only partially decomposed. G. Lunge and R. Schock conclude that this soln. contains an iodine compound analogous with *iodine bleaching powder*, or *iodide of lime*, Ca(IO)I. W. A. R. Wilks studied the action of soln. of chlorine, bromine, and iodine in carbon tetrachloride on dry slaked lime, and found that bromine is adsorbed until a maximum of adsorption is attained. In some cases a slight "superadsorption" is noticed. The colour of bromine bleaching powder is due to this adsorption product. The concentrations of bromine in soln. (C_2) and in lime (C_1) before the maximum of adsorption is reached are connected by the equation $C_1/C_2^{\frac{1}{3}}=k$. The amount of bromine adsorbed by slaked lime depends on the dryness of the lime. Similar results were observed in the case of iodine and lime. The value n in the formula $(C_1/C_2)^n=k$ is one-third, as with bromine, but the constant k is different for bromine and iodine. For the same specimen of lime the mol. ratio of iodine to lime at the maximum of adsorption is less than the corresponding ratio for bromine. Chlorine behaves quite differently from the other two halogens under the same conditions. Adsorption phenomena could not be detected, but the results indicate the formation of a chemical compound. Slight differences in the dryness of the lime have much greater effect on the absorption of bromine and iodine than on that of chlorine.

J. Walker and S. A. Kay showed that the brown product of the action of iodine in aq. or chloroform soln. on magnesia is a case of adsorption analogous to the adsorption of acids by silk, and of iodine by starch. P. Guichard studied the adsorption products with iodine vapour and alumina, silica, magnesia, and beryllia.

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§ 5. The Hypochlorites, Hypobromites, and Hypoiodites

In 1834, A. J. Balard[1] prepared solutions of salts of hypochlorous acid—the hypochlorites—by mixing the aq. acid with alkalies, magnesia, or with zinc or copper hydroxides, and avoiding an excess of the acid. If the liquids are not kept cold, the hypochlorites decompose into chlorides and chlorates. A. J. Balard said :

The presence of a certain excess of base prevents the conversion of the hypochlorite into chlorate and chloride, whereas it is rapidly effected when the acid is in excess. It is therefore necessary to add the acid to the alkaline substance in quantity insufficient for saturation, and constantly to agitate the bottle immersed in cold water ; and not to reverse the operation by gradually saturating the acid with the base. By taking these precautions, conc. soln. of hypochlorous acid and potash may be used without precipitating potassium chlorate, notwithstanding the sparing solubility of this salt. This proves that if any chlorate is formed, the quantity is very small.

If an excess of alkali be present, the soln. can be dried in vacuo at ordinary temp. without much decomposition. An excess of chlorine acting on hypochlorites at ordinary temp. liberates the acid: $KOCl+Cl_2+H_2O=KCl+2HOCl$. Similarly with bleaching powder. The liberated acid can be removed by distillation, but a rise of temp. is then attended by the formation of chloric acid. J. L. Gay Lussac (1842) dissolved two mol. of chlorine monoxide in a soln. containing a mol. of K_2O, and found that on evaporation in vacuo, the eq. of one mol. of chlorine monoxide was removed from the liquid; this indicates that the alkali hypochlorites contain the eq. of a mol. each of chlorine monoxide, Cl_2O, and potassium monoxide, K_2O. A. W. Williamson stated that hypochlorous acid does not expel carbon dioxide from the carbonates except by its own decomposition. W. Wolters, however, stated that carbon dioxide is expelled from sodium carbonate, and G. Lunge and H. Schäppi drove carbon dioxide from calcium carbonate by distilling hypochlorous acid with an excess of this salt.

If too little chlorine is passed into a soln. of sodium carbonate to produce an effervescence, the pale yellow liquid smells faintly of chlorine and first reddens and then bleaches turmeric paper; the liquid does not lose its bleaching power on boiling, but it does so on evaporation. If the soln. of sodium carbonate be sat. with chlorine, a yellow strongly bleaching liquid is obtained which when evaporated in thin layers in warm air, gives a residue which first browns, and then bleaches turmeric paper. Consequently sodium carbonate is still present. When the liquid is boiled, it loses its colour, and on evaporation furnishes sodium chloride, chlorate, and a little carbonate. According to W. R. Dunstan and F. Ransome, when chlorine is passed into an aq. soln. of sodium carbonate until the liquid is but faintly alkaline, the liquid contains no free hypochlorous acid, but sodium hypochlorite; when the soln. is faintly alkaline, it contains both sodium hypochlorite and free hypochlorous acid; with a still further quantity of chlorine, the liquid contains some sodium hydrogen carbonate, sodium chloride, and free hypochlorous acid, but no sodium hypochlorite, and it corresponds with the *liquor sodæ chloratæ* of the British Pharmacopœia. If the treatment with chlorine be continued until the evolution of carbon dioxide ceases, the soln. contains sodium chloride and chlorate and free hypochlorous acid.

When an aq. soln. of alkalies, alkaline earths, or magnesia is treated with chlorine gas, the so-called *bleaching liquor*, is obtained. Too high a temp. or an excess of chlorine gas makes the liquid unstable, because the contained hypochlorite then readily decomposes into chlorate and chloride. Several of these bleaching liquids have been given special trade names[2]—*e.g. extrait d'eau de Javelle; esprit de Javelle; chlorozone; chlorogen*, etc.—and extravagant claims have been made about their bleaching qualities. They can be regarded as modifications of the older *eau de Javelle*, or rather *eau de Labarraque* mixed in some cases with some bleaching powder. As G. Lunge puts it, they are "nothing but ordinary soln. of *chloride of soda* with some free alkali to make them fitter for carriage, and all assertions going beyond this are simply deceptions practised on the consumers."

Conc. soln. of sodium hypochlorite with up to 42 per cent. of available chlorine have been made under the trade name *chloros*, by passing chlorine into a soln. of caustic soda of such a strength that the sodium chloride which is formed separates out. The temp. is kept below 27°. The crystals of sodium chloride are removed, and more chlorine is introduced, but the sodium hydroxide is always kept in excess or the soln. will be unstable. A. J. Balard prepared potassium, sodium, and lithium hypochlorites by neutralizing a well-cooled soln. of the base with the acid. E. Soubeiran evaporated in vacuo the liquid obtained by treating a soln. of calcium hypochlorite with sodium carbonate, and obtained, before the liquid had all evaporated, crystals of sodium chloride and of sodium hypochlorite. P. Mayer and R. Schindler obtained solid potassium hypochlorite mixed with potassium hydrocarbonate by the action of chlorine—developed from 10 parts of sodium chloride—on a soln. of 24 parts of potassium hydrocarbonate and one of water.

They also obtained an analogous solid sodium hypochlorite by the action of chlorine—from 100 parts of sodium chloride—on 19 parts of sodium carbonate moistened with one part of water. M. Muspratt and E. S. Smith[3] prepared a conc. soln. of sodium hypochlorite by treating with chlorine a 35 per cent. soln. of sodium hydroxide, cooled by ice-water. The precipitated sodium chloride is removed, and sodium hydroxide added equivalent to the sodium chloride removed: The treatment with chlorine was continued until the soln. was about 5*N*. Sometimes there is a spontaneous transformation of hypochlorite to chlorate which is prevented by (i) working at a low temp.: (ii) maintaining an excess of alkali: and (iii) ensuring the absence of iron and other heavy metals which act as catalysts. If the conc. soln. of sodium hypochlorite so prepared be cooled to about −10°, needle-like crystals belonging to the cubic system separate out. Their analysis gives: 37·6 per cent. NaOCl; 3·7, NaCl; 58·7, H_2O; and no sodium chlorate. Their composition thus corresponds with **hexahydrated sodium hypochlorite,** $NaOCl.6H_2O$, or, according to M. P. Appleby, with *heptahydrated sodium hypochlorite*—the analyses agree with either. The crystals melt between 18°–21° by dissolving in their own water of crystallization, and then rapidly decompose. If the crystals be exposed to a current of dry air under reduced press., some of the water of crystallization can be removed, and the crystals do not melt below 43°. M. P. Appleby found that if the melted hepta- or hexa-hydrate be cooled slowly large deliquescent greenish-yellow crystals of **pentahydrated sodium hypochlorite,** $NaOCl.5H_2O$, are formed, which melt at 27°. M. Berthelot[4] gives for the heat of the reaction $Cl_2+K_2O_{soln.}=25·4$ Cals.; and for $Cl_2O_{soln.}+K_2O_{soln}=9·6$ Cals. For the reaction: $Br_{2 liquid}+2KOH_{soln.}=KBr_{soln.}+KOBr_{soln.}+72$ Cals. J. Thomsen gives: $NaOH_{aq}+HOCl_{aq.}=9·98$ Cals.; for $Cl_2+2NaOH_{aq.}=24·65$ Cals., and M. Berthelot gives 25·31 Cals. According to F. M. Raoult, the f.p. of a gram of sodium hypochlorite in 100 grms. of water is lowered 0·454°, so that the molecular lowering is 33·9. M. Bouvet noted that conc. soln. of this salt rapidly lose their activity in sunlight, and this occurs fastest in white glass bottles, and slower in brown glass bottles. He found a soln. in the shade or in darkness remain practically unchanged after four weeks.

K. Kraut[5] claimed to have prepared *lithia bleaching powder* analogous with ordinary bleaching powder. At 0° chlorine has no action on lithium hydroxide, but at a higher temperature a product is obtained analogous to that produced with lime. Lithia is a univalent base, and therefore lithia bleaching powder cannot be a mixed salt; but G. Lunge and P. Naef showed that K. Kraut's product with lithia is in all probability a mixture of **lithium hypochlorite,** LiOCl, and lithium chloride, LiCl, for it is scarcely acted upon by carbon dioxide at ordinary temperatures, and the gas which is evolved contains some chlorine monoxide—with bleaching powder chlorine gas in amounts corresponding with the equation: $Cl.Ca.OCl+CO_2=CaCO_3+Cl_2$ is evolved, and only a trace of chlorine monoxide.

A. J. Balard[6] prepared a soln. of **sodium hypobromite,** NaOBr, by working in a similar manner to the process employed for the hypochlorite. When bromine is gradually added to soda lye, the bleaching power increases up to a maximum, and after that decreases owing to the conversion of the hypobromite into bromate. A. J. Balard also described a similar product, **potassium hypobromite,** obtained by the action of bromine on potassium carbonate.

C. F. Schönbein, as previously indicated, found that when iodine water is mixed with potassium hydroxide, the analogy of the product with soln. of the hypobromites and hypochlorites shows that **potassium hypoiodite** is in all probability formed by a reversible reaction, $2KOH+I_2\rightleftharpoons KI+KOI+H_2O$, and that, when in equilibrium, the addition of potassium iodide will reverse the reaction, forming free iodine and potassium hydroxide. Hence, (i) the amount of potassium hydroxide required to complete the reaction must be greater than is indicated by the equation, as was found to be the case by R. L. Taylor; and (ii) the failure of many to obtain evidence of bleaching soln. of hypoiodite when soln. of iodine in potassium iodide are employed. If a large excess of potassium iodide is present, this will prevent

the formation of any but the smallest amouut of hypoiodite. E. Péchard found that when iodine acts on sodium hydroxide, a mixture of sodium iodide, sodium iodate, and sodium hypoiodite is formed, and that the iodide and hypoiodite react with the liberation of iodine. F. D. Chattaway and K. J. P. Orton assume that sodium hypoiodite is formed in an intermediate stage in the decomposition of nitrogen iodide by a soln. of sodium hydroxide.

When possibly sodium diparaperiodate, $Na_4H_4I_2O_{10}.H_2O$, or sodium iodate, $NaIO_3$, is calcined at not too high a temp., the residue with the composition Na_4I_2O was reported by F. Ammermüller and G. Magnus in the former case, and by J. von Liebig in the latter. There has been some controversy between C. Langlois, C. G. Latusch, and C. F. Rammelsberg, etc., as to whether sodium hypoiodite is an integral part of the compound; but the whole discussion is futile until the nature of the product has been more closely investigated.

A. J. Balard [7] found that when hypochlorous acid and aqua ammonia are mixed different phenomena are produced according to the concentration of the soln. When conc. well-cooled soln. are mixed, a white clond is produced and sometimes oily drops of the highly explosive nitrogen chloride are produced. When very dil. soln. are mixed, bubbles of nitrogen are given off, and the liquid rendered alkaline by ammonia still possesses the power of bleaching a soln. of indigo blue, but bubbles of nitrogen continue to be given off, the alkalinity disappears, and the liquid becomes acid when it no longer possesses the power of bleaching. Hence, adds A. J. Balard, the existence of **ammonium hypochlorite** is very probable; it is the ephemeral hypochlorite obtained by E. Soubeiran, by the action of ammonium carbonate upon a soln. of bleaching powder. The soln. gave off nitrogen, and when evaporated in vacuo, left a residue of ammonium chloride. C. F. Schönbein showed that the liquid produced by adding ammonia to chlorine water, until the soln. turned turmeric paper brown, possessed all the characteristic properties of an hypochlorite. C. F. Cross and E. J. Bevan prepared a similar product by the electrolysis of a soln. of ammonium chloride. According to J. Thiele, if the soln. be distilled in vacuo, the distillate possesses reducing qualities, the residue does not reduce. If the soln. be mixed with sodium hydroxide before distillation, the distillate does not exert a reducing action. It was therefore inferred that in the first case ammonium hypochlorite was distilled into the receiver, and in the second, the alkali fixed the hypochlorous acid and prevented its distillation. There are some different opinions as to the mode of action of chlorine on aqua ammonia—A. A. Noyes and A. C. Lyon believe that nitrogen trichloride (*q.v.*) is first formed, and this is hydrolyzed in dil. soln.: $NCl_3+2NH_4OH+H_2O=2NH_4OCl$. There are also differences of opinion as to the agent which effects the reduction—*e.g.* amongst R. Luther and N. Schilow, F. Raschig, J. Kolb, G. Lunge and R. Schoch, F. Dreyfus, etc. Some consider the proof of the existence of ammonium hypochlorite to be defective, for the alleged compound has not been isolated; its aq. soln. rapidly decomposes at ordinary temp.; and there are irregularities in its oxidizing action—for instance, while it acts like other hypochlorites on aniline salts, sulphites, arsenites, and potassium iodide, yet it does not bleach plant fibres, decolorize indigo, transform lead hydroxide into the peroxide, nor oxidize ferrocyanides in acetic acid soln. It must be remembered that the ephemeral ammonium hypochlorite must of necessity be present at the commencement in very dil. soln.—one or two per cent.

C. F. Schönbein also prepared **ammonium hypobromite** by a process analogous to that employed for the hypochlorite, and obtained a liquid with similar oxidizing properties. The liquid is assumed to contain a mixture of ammonium hypobromite and bromide. C. F. Schönbein likewise inferred the transient formation of **ammonium hypoiodite** when iodine water and aqueous ammonia are mixed, whereby the liquid is decolorized. The soln. gave a deep blue coloration with starch paste and potassium iodide, etc., and behaved like analogous soln. of the alkali

hypoiodites. F. D. Chattaway and K. J. P. Orton have discussed the formation of ammonium hypoiodite in the decomposition of nitrogen iodide by aqua ammonia.

R. Chenevix notes the ready solubility of cupric oxide in chlorine water, and P. Grouvelle found that the soln. obtained by passing chlorine into water with cupric oxide in suspension possessed bleaching properties, and these were retained even after the soln. had been boiled for a quarter of an hour. A. J. Balard found that the distillation of P. Grouvelle's liquor furnished some hypochlorous acid and a green oxychloride, $3CuO.CuCl_2.4H_2O$, was formed in the retort. A. J. Balard prepared a soln. of **cupric hypochlorite** by dissolving cupric hydroxide in hypochlorous acid. It is also made by the action of cupric sulphate on calcium hypochlorite. A. J. Balard found that copper filings are partially dissolved by hypochlorous acid, the soln. after standing some time contains cupric chloride, and deposits a green pulverulent cupric oxychloride.

L. N. Vauquelin found that when chlorine acts on silver oxide diffused in water, a mixture of silver chloride and chlorate is formed, and it was accordingly supposed that these same products are obtained when chlorine acts on the salts of silver. The products observed by L. N. Vauquelin were shown by A. J. Balard to be end products, being preceded by the formation of silver hypochlorite. According to A. J. Balard, finely divided silver immediately decomposes hypochlorous acid with the evolution of oxygen, and the formation of silver chloride. Again, if an alkali hypochlorite be treated with silver nitrate, or if silver oxide, Ag_2O, suspended in water, be treated with chlorine, much heat is developed and silver chloride and silver peroxide are precipitated while a liquid with bleaching properties is formed. The liquid is very unstable, and decomposes in a few minutes with the separation of silver chloride and the formation of a soln. of silver chlorate which does not bleach. If an excess of chlorine be employed, all the silver is precipitated and a soln. of hypochlorous and chloric acids remains. If an alkali hydroxide be added to the bleaching liquid, oxygen is evolved, and a mixture of silver chloride and peroxide is precipitated. Similar results are obtained if an aq. soln. of silver chlorate, nitrate, or acetate be employed except that the corresponding acid is liberated. J. S. Stas has shown that probably no chloric acid or silver chlorate is formed in the primary reaction: $Ag_2O+2Cl_2+H_2O=2AgCl+2HClO$. If the silver oxide or carbonate be in excess, the silver oxide gradually forms **silver hypochlorite,** $2HOCl+Ag_2O=2AgOCl+H_2O$, which is readily soluble, and the soln. is stable so long as it is shaken with the excess of silver oxide present. This salt is partially decomposed on standing in darkness, and completely decomposed at 60° into silver chloride and chlorate: $3AgOCl=2AgCl+AgClO_3$, and the latter remains in soln. in the alkaline liquid. J. S. Stas found no signs of the formation of perchloric acid. F. Raschig prepared silver hypochlorite by the action of alkaline sodium hypochlorite on silver nitrate, and also by adding a soln. of silver nitrate to sodium azide, NaN_3, or to a soln. of chloroazide in sodium hydroxide.

A. J. Balard found that gold or platinum are not affected by hypochlorous acid, either alone or mixed with sulphuric or nitric acid. The last-named mixture, however, would probably act on both metals owing to the formation of free chlorine. No *gold hypochlorite* has yet been prepared.

A. J. Balard [8] prepared an olive-green insoluble mass by the action of bromine water on copper oxide, vegetable colours are not bleached, but nitrogen is evolved from ammonia, and carbonic and other acids set free bromine. When heated, oxygen, bromine, and water are given off, and copper oxybromide remains. The solid is possibly a mixture of bromine and copper oxybromide and not **copper hypobromite**. A. J. Balard also prepared a soln. which probably contained **silver hypobromite** by the action of bromine water on silver oxide. The product easily decomposes into bromide and bromate. F. W. Schmidt suggested that the white flocculent precipitate obtained by the action of iodine on a very dil. ammoniacal soln. of silver nitrate is possibly **silver hypoiodite.**

The hypochlorites appear to be all very soluble in water, and they are so prone to decomposition that very few have been isolated.

In addition to soln. of chloride of lime—*lime bleach liquor*—bleaching liquids with magnesium, zinc, or aluminium hypochlorites as the active agents have also been made and special virtues claimed for their use. For example, if magnesium sulphate be added to a soln. of bleaching powder, calcium sulphate is precipitated and a soln.—*magnesia bleach liquor*—of magnesium hypochlorite can be decanted off; similarly with zinc hypochlorite—*zinc bleach liquor*; and with aluminium hypochlorite—*alumina bleach liquor*, or *Wilson's bleach liquor*.

In 1875, C. T. Kingzett [9] obtained feathery crystals of **tetrahydrated calcium hypochlorite,** $Ca(OCl)_2.4H_2O$, by the slow evaporation of a filtered soln. in vacuo over sulphuric acid and caustic potash; K. J. P. Orton and W. J. Jones obtained similar crystals from $4N$-soln. sat. with respect to this salt at temp. above 0°. C. T. Kingzett and F. Winteler also obtained crystals by cooling soln. of bleaching powder in a freezing mixture. The former did not obtain satisfactory analytical numbers, and the latter, without analysis, stated the crystals were calcium oxychloride. K. J. P. Orton and W. J. Jones also obtained large prismatic crystals of a basic hydrated compound of calcium chloride and hypochlorite from a $2N$-soln. of bleaching powder which had been left for some weeks in a cupboard in the dark in autumn and also by cooling to −18° in a freezing mixture. The ratio $CaCl_2$ to $Ca(OCl)_2$ in these crystals is nearly constant 1 : 1, but the calcium hydroxide varies very much. This shows that the base is associated with the compound as an isomorphous mixture, or else a number of different basic salts are in question. The latter hypothesis is not probable in view of the constancy of the ratio $CaCl_2 : Ca(OCl)_2$. H. Ditz obtained a substance corresponding with $CaO.Ca(OCl)Cl.H_2O$, *i.e.* $2Ca(OH)_2.CaCl_2.Ca(OCl)_2$ by the action of chlorine on calcium hydroxide at −10°. The Chemische Fabrik Griesheim-Elektron obtained a patent for the preparation of anhydrous crystals of calcium hypochlorite by a method similar to that employed by C. T. Kingzett. The anhydrous crystals, unlike the hydrated crystals of C. T. Kingzett, are less prone to decomposition than the best bleaching powder, and it is sold as *hyporit*. The same firm found that if a conc. soln. of slaked lime be chlorinated so that the sp. gr. of the filtered soln. is 1·15, compounds of calcium hypochlorite and hydroxide are precipitated on passing in more chlorine. It is said that there is a whole series of these basic hypochlorites or **calcium hydroxyhypochlorites**: $Ca(OCl)_2.nCa(OH)_2$, but only those with $n=2$ and $n=4$ have been analyzed. These sparingly soluble compounds form well-defined crystals which decompose with water, and they are said to be the cause of much of the milkiness of ordinary soln. of bleaching powder. The continued passage of chlorine attacks these basic hypochlorites, until finally calcium hypochlorite itself is precipitated either directly, or by the salting action of calcium chloride. It was once assumed that if the sp. gr. of lime bleach-liquor exceeded 1·15, the hypochlorite was converted into chlorate by further chlorination; but if slaked lime be added to a soln. of bleaching powder, the basic compounds are precipitated, and the precipitates dissolve by the passage of more chlorine; by repeating the addition of slaked lime, and treatment with chlorine, it is possible to make calcium hypochlorite soln. of any desired concentration short of the point where crystallized calcium hypochlorite is precipitated.

P. Grouvelle (1821) [10] observed that a mol. of barium hydroxide absorbs two gram-atoms of chlorine, forming a product from which all the chlorine is expelled by carbon dioxide in two days. A. J. Balard (1834) says that the direct combination of hypochlorous acid with the powerful bases is accompanied by the development of much heat, and if the temp. is allowed to rise, the hypochlorite which may be formed changes into chlorate and chloride. By neutralizing a well-cooled soln. of the base with hypochlorous acid, A. J. Balard prepared soln. of **calcium, strontium, and barium hypochlorites**, the existence of which, he said, is incontestable; and added that calcium and barium hypochlorites serve for the preparation of other hypo-

chlorites, by double decomposition. B. C. Brodie (1862) found that hydrogen peroxide furnishes oxygen when treated with a soln. of chlorine in baryta water through which air has been passed to drive off the free chlorine. C. Göpner (1873) says that when hexahydrated barium hydroxide is treated with dry chlorine, dihydrated barium chloride is formed as well as a product containing 28·5 per cent. of free barium hydroxide, and 29·33 per cent. of active chlorine. E. Schwarz found that baryta and strontia furnish products analogous to ordinary lime bleaching powder (*q.v.*).

J. J. Berzelius[11] evaporated in vacuo a mixture of theoretical amounts of bromine and calcium hydroxide, and obtained a dry odourless red mass supposed to be a mixture of calcium bromide and **calcium hypobromite,** $Ca(BrO)_2$, together with some calcium bromate. The aq. soln. is yellow, and possesses bleaching qualities. A. J. Balard obtained similar results. According to C. Löwig, when the red solid is heated, it loses bromine, and then oxygen. Acids even so weak as carbonic acid, drive off the bromine. With silver nitrate a white precipitate is obtained which rapidly blackens in light. A. J. Balard obtained similar evidence of the formation of **strontium hypobromite**, and of **barium hypobromite**. The soln. lose their bleaching properties in light, when heated, and when treated with an excess of bromine—barium bromate, $Ba(BrO_3)_2$, is then precipitated. M. Berthelot gives for the heat of formation at 13° with one eq. in six litres of water, $BaO+Br_2=11·4$ Cals. According to J. S. Arthur and L. G. Killby, when the red bromine compound is heated to 100°, a bactericidal compound—*calcium oxy-hypobromite*, $CaO.CaOBr_2.H_2O$—stable up to 100°, is formed as a pale yellow powder containing about 33 per cent. of available bromine, and with properties similar to bleaching powder. W. Knop has studied the action of nitrogen compounds on barium hypobromite.

J. L. Gay Lussac found that iodine vapour is absorbed by heated calcium oxide without the evolution of oxygen, and P. Grouvelle noted that the iodine is driven off if the temp. is raised still higher. C. F. Rammelsberg found that 3 per cent. in weight is lost by the treatment. J. J. Berzelius evaporated in vacuo at 30° a mixture of iodine and calcium hydroxide so long as iodine was given off. A black mass was obtained which forms a dark brown soln. with water. There is nothing here to show that the iodine is merely absorbed or adsorbed by the calcium oxide. G. Lunge and R. Schoch obtained a bleaching liquid—presumably containing **calcium hypoiodite,** some iodate, and iodide—by treating calcium hydroxide with iodine and water at ordinary temp. The soln. is not very stable; it gradually changes in darkness, in light or when heated the change is more rapid still. R. L. Taylor showed that if iodine and lime are rubbed together with a little water, and diluted at once, instead of standing some hours before dilution as recommended by G. Lunge and R. Schoch, better results are obtained, for the soln. then exhibits the characteristic reactions of the alkali hypoiodites.

P. Grouvelle (1821) obtained a bleaching liquid by passing chlorine gas into water containing magnesia in suspension. He noted that the bleaching power was not all destroyed by boiling the liquid for a quarter of an hour. On evaporation to dryness, the product decomposed into chlorine and magnesium oxide. A. J. Balard (1834) prepared a soln. of **magnesium hypochlorite** by the action of hypochlorous acid on magnesium oxide, which, in the presence of an excess of acid gradually decomposed into a mixture of magnesium chloride and chlorate with the evolution of some oxygen. In the presence of an excess of the base, in vacuo, a similar decomposition occurs. G. Lunge and L. Landolt allowed chlorine to act on water with suspended magnesia, or in dry magnesium hydroxide, at 0°, and in the latter case they did not obtain a product like bleaching powder, but rather a mixture of magnesium chloride and hypochlorite. The hypochlorite is also formed at 15°, but at 70° nearly all is converted into chlorate. P. Bolley and M. Jokisch prepared magnesium hypochlorite by the action of magnesium sulphate on a soln. of bleaching powder, and A. D. White, by dissolving magnesium metal in hypochlorous acid.

G. Kereszty and E. Wolf passed chlorine into an aq. suspension of magnesia, and obtained what they regarded as a basic magnesium hypochlorite; the most favourable temp. is between 20° and 22°. Practically no chlorate is produced if, after the introduction of the chlorine, the reacting mixture is allowed to stand for a considerable time, or be heated to 80° and kept at that temp. for 6 to 8 hrs. in the dark. The precipitate is thoroughly washed with hot water, and dried with the exclusion of carbonate dioxide. C. F. Cross and E. J. Bevan found that a white substance is formed at the cathode during the electrolysis of a soln. of magnesium chloride; unlike magnesium hypochlorite, this substance is not soluble in water, and it is stable. Similar substances were obtained during the electrolysis of magnesium bromide and iodide.

P. Grouvelle obtained a similar result to that obtained with magnesium oxide by treating zinc oxide suspended in water with chlorine gas; and A. J. Balard found that when the liquid was distilled some hypochlorous acid collected in the distillate, while zinc chloride remained in the retort, where also some zinc oxychloride was precipitated. As with magnesium hypochlorite, A. J. Balard likewise formed a soln. of **zinc hypochlorite** by the action of hypochlorous acid on zinc oxide. The soln. behaved in an analogous manner when the attempt was made to concentrate it in vacuo. A. J. Balard also prepared a similar soln. by double decomposition of zinc sulphate and an excess of calcium hypochlorite. G. Lunge and L. Landolt obtained a soln. of zinc hypochlorite by a process similar to that employed by P. Grouvelle. They found that some chlorate was formed when working at 15°, and still more at higher temp. The zinc hypochlorite was found to decompose into zinc chloride or oxychloride and oxygen. Very little chlorate is present in the soln. obtained by decomposing zinc sulphate with a soln. of bleaching powder. The soln. of zinc hypochlorite is less stable than that of the calcium or magnesium salt. R. Böttger found that hypochlorous acid has no appreciable action on zinc.

By shaking bromine water with finely divided magnesia, C. Löwig obtained a yellow liquid which at first behaved like an alkali towards litmus, but a more protracted action removed the colour, and when treated with weak acids gave off bromine. It is therefore supposed to be a soln. of **magnesium hypobromite**. A. J. Balard found that the soln. is decomposed by exposure to light, heat, or by evaporation in vacuo, and with an excess of bromine is converted into magnesium bromide and bromate.

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A. J. Balard found mercury immediately decomposes hypochlorous acid without the disengagement of any gas, but mercury oxychloride is formed. P. Grouvelle reported previously that when chlorine acts on mercuric oxide suspended in water, mercury oxychloride, very slightly soluble in cold water, is formed. L. J. Thénard found that the liquid contained both chloride and chlorate of mercury, also in soln. A. J. Balard, however, believed that these bodies are "formed consecutively, and that their existence was preceded by that of a *mercuric hypochlorite*, as takes place with the salts of silver," and, as previously indicated, he prepared hypochlorous acid by the action of chlorine on mercuric oxide suspended in water. No mercury hypobromite has yet been isolated. There is a possible formation of **mercury hypoiodite**, or more probably of hypoiodous acid, when iodine is shaken up with

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P. Grouvelle [14] reported that aluminium hydroxide suspended in water through which chlorine was passed does not go into soln. Z. G. Orioli obtained a bleaching liquid by the decomposition of a soln. of bleaching powder with aluminium sulphate, and G. Lunge and L. Landolt found that any *aluminium hypochlorite* which may be formed immediately decomposes, liberating hypochlorous acid. A. D. White also found that aluminium is slowly attacked by hypochlorous acid, and the resulting aluminium hypochlorite immediately decomposes into aluminium hydroxide, oxygen, and chlorine.

Iron filings immediately decompose hypochlorous acid with a brisk effervescence produced by the evolution of chlorine; the iron is partly oxidized and in part dissolved as chloride without the formation of any chlorate. A. J. Balard commented on this: "The greater number of other metallic substances do not decompose hypochlorous acid, and I am yet entirely ignorant of the cause of the peculiar behaviour of iron." P. Grouvelle passed chlorine through water with iron hydroxide in suspension and a bleaching liquid along with ferric chloride was produced, and he found the liquid retained its bleaching properties after boiling for a quarter of an hour; but A. J. Balard failed to confirm this statement: he could not make *ferric hypochlorite* either (i) by the action of hypochlorous acid on iron hydroxide, for hypochlorous acid does not dissolve ferric oxide; or (ii) by the action of calcium hypochlorite on ferric sulphate, for calcium sulphate and ferric oxide are produced. Hence, adds A. J. Balard, "ferric hypochlorite cannot exist;" the results by P. Grouvelle are due to the formation of ferric chloride and hypochlorous acid in dil. soln.: when the mixture was heated, a portion of the acid distilled off, and the reaction which occurred with the cold soln. was reversed, for ferric oxide and chlorine were formed. Ferrous oxide is oxidized to ferric oxide by hypochlorous acid.

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§ 6. Electrolytic Processes for the Preparation of Hypochlorites, Hypobromites, and Hypoiodites

Electrolytic bleaching liquids are also prepared by the electrolysis of soln. of sodium chloride. The cost with dil. soln. is about the same as with bleaching powder, but with more conc. soln. the cost with the electrolytic bleaching liquid is rather greater than with bleaching powder. Consequently, for laundry bleaching, fine textile bleaching, and other cases where dil. soln. are used, the electrolytic bleach is preferred, but this is not the case where conc. soln. are used—*e.g.* paper pulp bleaching, sewage treatment, etc. The electrolytic bleaching liquor is more rapid in its action than chloride of lime ; washing with acid is not necessary since there are no lime salts to remove ; and there is less likelihood of irregularity in composition and in action.

In 1851, C. Watts [1] patented a process for preparing chlorine, soda, hypochlorites, and chlorates by the electrolysis of soln. of alkali chlorides ; but little progress was made for many years. In 1882, A. P. Lidoff and W. Tichomiroff described the preparation of hypochlorites by this process, and in 1883, E. Hermite patented a process, for the preparation of electrolytic bleaching liquor, which has been used in several countries, but is now regarded as an obsolete process.

In E. Hermite's cell, the cathode was made of zinc discs supported on two slowly rotating shafts running through each cell, and separated from one another by a partition.

The anodes were made of thin sheets of platinum held in a non-conducting frame between the zinc discs. Sea water was early used as an electrolyte, and later a 5 per cent. soln. of sodium chloride with about one per cent. of magnesium chloride. The electrolyte was kept in circulation by means of a special pump.

Numerous other types of cell have been devised, and several of these have a much greater efficiency than the Hermite cell—e.g. K. Kellner's,[2] Schuckert and Co.'s, M. Haas and F. Oettel's, and P. Schoop's systems. The electrolytic production of chlorine and caustic soda, of bleaching liquors, and of disinfecting liquid—e.g. the so-called Dakin's solution—are growing industries.

In K. Kellner's cell, the electrodes are made of glass or other non-conducting material with wire or strips of an alloy of platinum-iridium fixed on the surface. These plates are arranged vertically side by side in a stoneware or glass trough so as to divide the cell into a number of narrow compartments. The brine enters the cell through two inlets in the bottom and flows upwards between the narrow plates, where it is electrolyzed by the current which enters and leaves the cell by two conducting plates placed at opposite ends of the cell. The wire gives a current of high density. The electrolyzed brine escapes through slits in the walls on opposite sides of the cell. V. Hölbling, in his *Die Fabrikation der Bleichmaterialien* (Berlin, 1902), describes the installation of Siemens and Halske. A stream of water trickles through a cylinder packed with salt, and the issuing brine is filtered through a cloth, whence it passes into a tank, where it is mixed with sufficient water to give it the correct specific gravity. The brine thence passes to a storage tank, whence it is run as required to another tank *A*, Fig. 4, which contains a leaden worm piping in order to keep the temp. of the brine low. The electrolytic cell *C* is fixed above the tank *A*. A pump *P* sucks the brine along *B*, and forces it through *D*, while the tap *E* is turned to shut off connection with *F*. The brine rises in the cell, and the electrolyzed liquid runs back into the tank *A*. This circulation of the brine is continued until the liquid contains the desired quantity of bleaching chlorine, when the stopcock *E* is turned and the bleaching liquor forced by the pump through *F* to the storage tank.

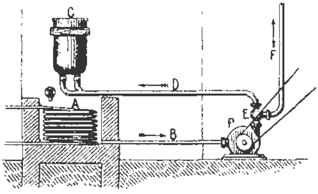

FIG. 4.—Arrangement for Preparation of Bleaching Liquor.

The work of F. Förster and E. Müller, described in the former's *Electrochemie wässeriger Lösungen* (Leipzig, 1917),[3] has shown that when a 10 per cent. aq. soln. of sodium chloride is electrolyzed between platinum electrodes, hydrogen and sodium hydroxide are produced at the cathode, and chlorine at the anode. The discharge potential of Na$^{\cdot}$-ions is $-2{\cdot}72$ volts, and this is much greater than $-0{\cdot}4$ volt, the discharge potential of H$^{\cdot}$-ions, so that hydrogen is preferentially discharged, and that even from a strongly alkaline soln. Consequently, although requiring a certain over-voltage, the production of hydrogen during the electrolysis of a soln. of sodium chloride is primary and not secondary. These relations can be reversed by discharging the sodium, not as a pure metal, but as an alloy with a cathode of, say, mercury, tin, or lead; or by using a cathode metal which has a high hydrogen over-voltage. For a sat. soln. of chlorine at atm. press. (0·064 mol. per litre), and normal with respect to Cl$'$-ions, the discharge potential is $-1{\cdot}667$ volts, and chlorine cannot be liberated at atm. press. if the potential difference is less than this value. With an acidic soln., normal with respect to H$^{\cdot}$-ions, hydrogen is liberated at $-0{\cdot}277$ volt. Although a soln. of sodium chloride is neutral at the commencement of the electrolysis, it becomes increasingly alkaline as the electrolysis progresses; this diminishes the concentration of the H$^{\cdot}$-ions. If the soln. of alkali hydroxide about the cathode be assumed normal, the discharge potential will be 0·54 volt. The cell will then have a voltage $0{\cdot}54-(-1{\cdot}667)=2{\cdot}2$ volts. The decomposition potential for the continuous electrolysis of a conc. soln. of sodium chloride requires 2·1 to 2·3 volts. Hydroxyl ions are liberated in

a *normal hydroxide soln. with a potential* $-1 \cdot 16$ *volts, and there is therefore a difference of nearly 0·5 volt between the discharge potential* of chlorine and hydroxyl ions, and oxygen not chlorine would therefore be the product of the electrolysis of strongly alkaline soln. of sodium chloride were it not for the fact that the potential of an anode from which oxygen is liberated steadily increases up to the point at which chlorine is set free.

If during the electrolysis of a soln. of sodium chloride, cathodic sodium hydroxide and anodic chlorine are desired, the anode and cathode liquids must be prevented from mixing by means of a diaphragm as in the electrolytic processes for chlorine; while if hypochlorite, chlorate, or perchlorates be the desired products, the anodic and cathodic liquids must be continuously mixed. *The chlorine from the anode* then reacts with the hydroxide from the cathode, forming the alkali hypochlorite. *If the mixing of the liquid is good, the reaction*: $Cl_2+2NaOH=NaOCl+NaCl+H_2O$, is almost quantitative. There will be a tendency for the chlorine to accumulate about the cathode, and in that case, there will be a high concentration of hypochlorite in that neighbourhood, and a corresponding tendency to form sodium chlorate: $3NaOCl=NaClO_3+2NaCl$, at the anode. The amount of chlorate formed about the anode will be less the better the circulation and the lower the temp. of the electrolyte. The rate of decomposition of the neutral hypochlorite is small, and the action would proceed until the soln. becomes sat. with sodium hypochlorite were it not for the nascent hydrogen produced on the cathode exerting a reducing action on the hypochlorite whereby the oxidized salt, NaOCl, is reduced back to the chloride: $2NaOCl+2H_2=2NaCl+2H_2O$. Consequently, the concentration of *the hypochlorite will reach a maximum value* and *remain stationary when the* rate of formation of hypochlorite about the anode is equal to its rate of reduction about the cathode.

In 1898, P. Imhoff discovered the important fact that the reduction at the cathode can be prevented by adding a very small proportion of potassium bichromate, $K_2Cr_2O_7$, to the electrolyte, and E. Müller showed that the chromate about the cathode is reduced to chromium chromate, $Cr_2(CrO_4)_3$, which forms an insoluble film on the cathode and prevents the soln. coming into actual contact with the electrode and into the sphere of action of nascent hydrogen. If the electrolyte be *strongly acid or alkaline, the film is dissolved, and the action of the anti-reducing* agent is either prevented or retarded. Vanadium salts, sodium resinate, and, as A. Thiele has shown, organic non-aromatic sulphur compounds in the presence of calcium salts can be used as anti-reducing agents in a similar manner.

*There is another reaction which limits the possible concentration of the hypo*chlorite in the electrolyte, namely, the electrolysis of the dissolved hypochlorite resulting in the liberation of oxygen and chlorine: $4ClO'+2H_2O=4HCl+3O_2$; and $2HCl=H_{2\text{cathode}}+Cl_{2\text{anode}}$, and the simultaneous formation of chlorate: $2ClO'+H_2O=2HClO_3$. Symbolizing these two reactions by one equation: $6ClO'+3H_2O=6H^{\cdot}+2ClO_3'+4Cl'+1\frac{1}{2}O_2$. This reaction—anodic chlorate formation—occurs only at the anode and not throughout the electrolyte. In the stationary state, therefore, when the concentration of the hypochlorite is a maximum, the rate of formation of the hypochlorite less the rate of its reduction at the cathode will be equal to the rate of electrolysis of the hypochlorite. The discharge of the six ClO′-ions requires the passage of 12 coulombs of electricity; so that in the stationary state, two-thirds of the current will be spent in producing chlorine which reacts with the alkali hydroxide to form hypochlorite, and one-third in the electrolysis of the hypochlorite. *Otherwise expressed, 66·6 per cent. of the current will* be spent in the production of *available oxygen* in the form of sodium chlorate, $NaClO_3$, and 33·3 per cent. in the production of *free oxygen*. This fact has been established by experiments with brine over a wide range of concentration, current density, and temp.

The reduction of the hypochlorite at the cathode, and the chlorate formation at the anode, become more difficult by *increasing the current densities at these electrodes*,

for the greater the quantity of chlorine coming from the anode, the less the opportunity of the hypochlorite reaching the anode; and, likewise, the smaller the cathode, the less chance will the hypochlorite have of coming in contact with the nascent hydrogen. The resistance of the more conc. soln. is less. The maximum hypochlorite concentration is less in dil. than in conc. soln. of sodium chloride because in the former case the hypochlorite must carry relatively more current. The resistance of the more conc. soln. is less. E. Müller (Fig. 5) illustrates the electrolysis of a neutral 4·37*N*-soln. of sodium chloride with a current density on the anode of 0·075 amp. and on the cathode 0·18 amp. per sq. cm. The concentration of the hypochlorite and chlorate oxygen is in grams per 100 c.c., the current yield, etc., are expressed in terms of the percentage of active oxygen. It will be seen that the concentration of the chlorate is very low at first, but that it increases as the concentration of the hypochlorite becomes constant, showing that hypochlorite is probably one of the first products of the electrolysis, and the starting-point for the formation of the chlorate, and for the evolution of oxygen.

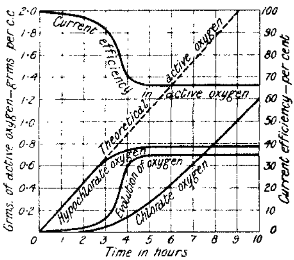

FIG. 5.—E. Müller's Curves showing the Electrolysis of Sodium Chloride Solutions.

If the soln. of sodium chloride to be electrolyzed is acidified with hydrochloric acid, the acid is first electrolyzed, and this continues until the soln. is nearly neutral, but the trace of hydrochloric acid which escapes electrolysis liberates hypochlorous acid, which then decomposes and increases the yield of chlorate. If acid be added to the soln. before the hypochlorous acid has attained its maximum concentration, all the hypochlorous acid in soln. is oxidized to chlorate, and if the addition of acid be similarly continued, 90 per cent. of the theoretical yield of chlorate can be obtained. Similar results can be obtained by keeping the soln. slightly acid by the addition of potassium acid fluoride, KHF_2, or alkali bicarbonate.

If the soln. of sodium chloride be made alkaline by the addition of alkali hydroxide the maximum concentration of the hypochlorite becomes less as the alkalinity of the soln. is increased and the chief products of the electrolysis are chlorate and free oxygen. The relative yields of hypochlorite and chlorate during the electrolysis of soln of 200 grms. of sodium chloride, and various amounts of the hydroxide per litre of soln., are indicated in Fig. 6, with an anode current density of 0·04 amp per sq. cm. It is assumed that the reaction representing the formation of chlorate in neutral, and in slightly and in strongly alkaline soln. is: $6ClO'+3H_2O=2ClO_3'+4Cl'+6H^{\cdot}+1\frac{1}{2}O_2$, but that in strongly alkaline soln., the chloride and hydroxyl ions react immediately on the anode to form hypochlorite. The higher hypochlorite concentration on the anode increases the production of chlorate; and when the alkalinity exceeds a certain value, the hydroxide is also electrolyzed, and the hydroxyl ions discharged at the anode reduce the yield of chlorate below the maximum indicated in Fig. 6. The effect of temp. on neutral soln. decreases the hypochlorite maximum, but in strongly alkaline soln. it increases the maximum.

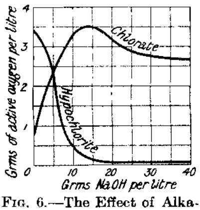

FIG. 6.—The Effect of Alkalinity on the Electrolysis of a Solution of Sodium Chloride

To summarize: the production of sodium hypochlorite is favoured by (i) Neutral conc. soln. of sodium chloride; (ii) Low temp.; (iii) High anodic current density; (iv) The presence of potassium bichromate; and (v) An adequate circulation of the electrolyte. G. E. Cullen and R. S. Hubbard have studied the best

conditions for the production of a dil. soln. of sodium hypochlorite to be used as Dakin's solution.

R. Lorenz and H. Wehrlin have also shown that the use of platinized platinum electrodes increases the maximum concentration of the hypochlorite. Carbon electrodes have a 10 to 28 per cent. porosity; and the soln. which fills the pores is electrolyzed, but the dissolved salt in the pores cannot be renewed as rapidly as the soln. about the surface of the electrode, and consequently the evolution of oxygen and the production of chlorate begin sooner, and the maximum concentration of the hypochlorite is less than with platinum electrodes. Part of the oxygen also oxidizes the carbon, and this makes the electrolyte slightly acid, thus favouring chlorate production.

Hypobromites.—During the electrolysis of soln. of an alkali bromide,[4] free bromine and oxygen are discharged at the anode, and the bromine unites with the sodium hydroxide formed at the cathode, producing alkali hypobromite. As in the analogous formation of hypochlorites, the concentration of hypobromite increases up to a maximum when any further electrolysis furnishes bromate. The free oxygen, derived from the hydroxide produced by the hydrolysis of the hypobromite, is evolved at the anode in increasing quantities as the concentration of the hypobromite increases. Alkali bromate is produced (*a*) by the secondary oxidation of alkali hypobromite by hypobromous acid: $NaOBr+2HOBr=HBrO_3+HBr+NaBr$; and (*b*) by the direct oxidation of the hypobromite: $HOBr+O_2=HBrO_3$. Unlike the analogous case with hypochlorites, there is virtually no electrolysis of the hypobromite. The conditions favouring the formation of hypobromites resemble those with hypochlorites. H. Pauli has shown that, excepting cases where a chromate is used to prevent reduction on the cathode, both bromates and hypobromites are reduced on a smooth platinum cathode.

Hypoiodites.—In the electrolysis of a soln. of alkali iodide,[5] the iodine liberated at the anode unites with the alkali hydroxide from the cathode to form hypoiodite. The very rapid hydrolysis of the hypoiodite leads to the formation of iodate: $2HIO+KIO=KIO_3+2HI$, and this even in alkaline soln. The result is analogous with that obtained with slightly acid soln. of hypochlorites, so that the hypoiodide quickly reaches a limiting maximum concentration—dependent on the concentration of iodide and iodate, the current density, and the temp.—when the product is exclusively iodate. Increasing alkalinity increases the maximum concentration of the hypoiodite, but decreases that of the hypochlorite. This difference arises from the different ways the iodate and chlorate are formed in the two cases. Since hypoiodites can never become very conc., the amount of hypoiodite electrolyzed is therefore very small; accordingly, the evolution of oxygen at the anode is entirely due to the electrolysis of the hydroxide, and is not concerned with the formation of iodate.

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§ 7. Chlorine, Bromine, and Iodine Trioxides; and the Corresponding Acids

A greenish-yellow gas supposed to be **chlorine trioxide,** Cl_2O_3, or *chlorous anhydride*, was prepared by N. A. E. Millon[1] in 1843, and described in his *Mémoire sur les combinaisons oxygènes du chlore.* The gas was made by the partial reduction of chloric acid, $HClO_3$, with a mixture of arsenious oxide, As_2O_3, and dil. nitric acid. It was supposed that the nitric acid was reduced to nitrogen trioxide, N_2O_3, simultaneously with the oxidation of the arsenious acid, H_3AsO_3, to arsenic acid, H_3AsO_4. The chloric acid was reduced by the nitrogen trioxide to chlorine trioxide, as the nitrogen trioxide simultaneously reoxidized to nitric acid: $2HClO_3+N_2O_3=Cl_2O_3+2HNO_3$. Several other methods of reduction were employed—*e.g.* M. Brandau reduced the chloric acid directly with arsenic trioxide without the use of nitric acid; J. Schiel used cane sugar; L. Carius, benzene; and T. Hermann, naphthalene. W. Spring also claimed to have made the gas by the action of chlorine on silver chlorate, $AgClO_3$. The gas product of these reactions, supposed to be chlorine trioxide, was analyzed, its density determined, and its properties tabulated. The results obtained by different observers did not agree. K. G. Thurnlackh showed that the general properties of the supposed chlorine trioxide ran parallel with those of chlorine dioxide; he found that when the gas is decomposed by heat it undergoes an expansion which is equal to half the volume of oxygen set free. If the gas were Cl_2O_3, the volume of oxygen set free should be equal to the observed expansion: $2Cl_2O_3$ (2 vols.)$=2Cl_2$ (2 vols.)$+3O_2$ (3 vols.). The corresponding result for chlorine dioxide, ClO_2, is: $2ClO_2$ (2 vols.)$=Cl_2$ (1 vol.)$+2O_2$ (2 vols.). K. G. Thurnlackh therefore concluded that the supposed chlorine trioxide or chlorous anhydride is a mixture of chlorine and chlorine dioxide with a little oxygen and carbon dioxide. The calculated density of chlorine trioxide Cl_2O_3, (air unity), is 4·1, and M. Brandau obtained 4·07 at 9°; 3·17 at 16°; N. A. E. Millon and J. Schiel obtained between 2·6 and 2·7. W. A. Miller (1845)[2] and D. Gernez (1872) reported that the absorption spectra of chlorine trioxide and chlorine dioxide are identical, while chlorine monoxide gave no bands. As A. Schuster remarks:

> As no other case is known in which two different compounds give the same spectrum, and as the oxides of chlorine are very unstable, there is no doubt that the spectrum of one of them only was observed, that gas to which the spectrum belongs being also present when the other oxide was examined.

D. I. Mendeléeff noted that a mixture of equal volumes of chlorine, chlorine di- and tri-oxides has a density corresponding with the value observed by N. A. E. Millon, and therefore inferred that Millon's gas "probably contains a mixture of approximately equal volumes of chlorine dioxide, ClO_2, chlorine trioxide, Cl_2O_3, and chlorine." There is, however, no unimpeachable evidence which justifies even this assumption; and it is now suppposed that the existence of the chlorine trioxide, the anhydride of chlorous acid, has not been established.

Chlorous acid.—The acid liquid obtained when chlorine dioxide, ClO_2, is dissolved in water is a mixture of chloric acid, $HClO_3$, and **chlorous acid,** $HClO_2$.

The reaction is symbolized: $2ClO_2+H_2O=HClO_2+HClO_3$, so that the aq. soln. of N. A. E. Millon's chlorine trioxide will contain a mixture of chloric and chlorous acids and chlorine, and a soln. of the same gas in alkali lye will contain a mixture of the alkali hypochlorite, chlorite, chlorate, chloride. The chlorites are accordingly formed when soln. of chloric acid, $HClO_3$, or chlorine dioxide, ClO_2, are partially reduced by the methods employed for the preparation of chlorine di- and tri-oxides. J. E. de Vrij [3] prepared the acid by reducing chloric acid with tartaric acid. G. Bruni and G. Levi used oxalic acid:

A mixture of 150 parts of oxalic acid, 40 of potassium chlorate, and 20 of water is heated to 60°, and the soln. conc. in vacuo at 50° until it begins to crystallize. The cold liquid is then treated with 3 volumes of absolute alcohol, when potassium carbonate is precipitated. Fine deliquescent needles of potassium chlorite can be obtained by *fractional* crystallization in vacuo. The residue gives a further crop of crystals of the chlorite by treatment with 95 per cent. alcohol. Small yellow crystals of silver or lead chlorites can be obtained by double decomposition.

J. L. Gay Lussac also noted the formation of calcium chlorite when bleaching powder—solid or solution—is decomposed in sunlight. K. G. Thurnlackh and K. F. von Hayn prepared a mixture of potassium chlorite and chlorate by the action of chlorine dioxide on potash lye: $2ClO_2+2KOH=KClO_2+KClO_3+H_2O$. A. Reychler found that if sodium peroxide is mixed with an aq. soln. of chlorine dioxide, the yellow colour of the soln. disappears as soon as sufficient sodium peroxide has been added, and the amount of oxygen evolved corresponds with the reaction: $Na_2O_2+2ClO_2=2NaClO_2+O_2$; and G. Bruni and G. Levi prepared barium chlorite by the action of a mixture of chlorine and carbon dioxides, free from chlorine, upon barium peroxide suspended in a soln. of hydrogen peroxide. The liquid was extracted with alcohol; the extract treated with an excess of ether; and the precipitated chlorite rapidly dried to free it from traces of ether and alcohol. With rapid filtration and drying, the barium chlorite, $Ba(ClO_2)_2$, is obtained virtually free from chloride. B. Carlson and J. Gelhaar stated that appreciable quantities of chlorite are formed in the electrolytic production of chlorates, but F. Förster and P. Dolch have shown that the merest traces are formed, and that the test employed by the former was vitiated by the presence of bromides. F. Förster and P. Dolch, as previously indicated, regard sodium chlorite as an intermediate product in the conversion of hypochlorites to chlorates.

A colourless aq. soln. of the free acid is obtained by treating barium chlorite with $\frac{1}{10}N$-sulphuric acid. When acidified with dil. sulphuric acid, there is a slow decomposition with the formation of chlorine dioxide, and the appearance of a yellow soln. may be regarded as a test for the presence of chlorites. This decomposition is hastened by the presence of chlorides and hypochlorites, and retarded by a small proportion of arsenious oxide, so that in this latter reagent the soln. remains colourless over an hour. It is highly probable that the colourless soln. contains hypochlorous acid. The hypochlorous acid in soln. probably reacts slowly with chlorous acid, forming chlorine dioxide: $HClO+2HClO_2=2ClO_2+HCl+H_2O$. The reaction is of the second order. Hence it may be that pure chlorous acid is fairly stable. The reaction between chlorous and chloric acids is not of the balanced type, since other substances besides chlorine dioxide are produced, and the proportion of chlorate in the system continually increases: $3HClO_2=2HClO_3+HCl$, and possibly also: $8HClO_2=Cl_2+6ClO_2+4H_2O$.

The reaction: $2ClO_2+2KOH=KClO_2+KClO_3+H_2O$, makes it appear as if chlorine dioxide is a mixed anhydride of chloric and chlorous acids. According to W. Bray, the reaction progresses in accord with the equation: $d[ClO_2]/dt=k[ClO_2]^2[KOH]$, where the bracketed symbols refer to molecular concentrations. It is therefore assumed that the primary reaction is $2ClO_2+KOH=KClO_3+HClO_2$, followed by the rapid: $HClO_2+KOH=KClO_2+H_2O$. The end of the reaction: $2ClO_2+2KOH=H_2O+KClO_2+KClO_3$, is recognized by the decolorization of the

soln. The product is comparatively stable, since W. Bray could recognize no change in the oxidation value of the soln. after six months. W. Bray also found that when a soln. of chlorine dioxide is treated with sodium acid carbonate, $NaHCO_3$, there is a very slow reaction: $2NaHCO_3+2ClO_2+H_2O=NaClO_3+NaClO_2+2H_2CO_3$, which occupies some weeks in darkness at 0°.

The chlorites.—Chlorous acid is monobasic, and forms salts of the type $M'ClO_2$, and also red acid salts which have not been isolated in the solid state. The salt of the alkalies and alkaline earths are colourless and hygroscopic. All the chlorites are soluble in water—the lead and silver salts are but sparingly soluble. The soln. undergo no appreciable hydrolysis. The chlorites are also fairly soluble in alcohol. G. Bruni and G. Levi determined the electrical conductivity of aq. soln. of potassium, silver, and barium chlorites, at 25°. The mobility of the chlorite ion, ClO_2', is between 50·6 and 51·7, so that the ion mobilities of the oxychlorine ions are: ClO_2', 51·0; ClO_3', 63·4; ClO_4', 73·6, showing that the ionic mobility increases with increasing oxygen content; the reverse obtained with the oxy-nitrogen ions—*e.g.* NO_2', 75·4; NO_3', 70·6. The degrees of ionization of potassium chlorite determined by cryoscopic measurements are respectively $a=0·930$; $a=0·920$; $a=0·935$; and $a=0·959$ for soln. containing 1·0656 grms. of salt per 10, 15, 20, and 40 grms. of water. The soluble chlorites form caustic soln. which bleach vegetable colouring matters, indigo blue, etc., even after the addition of arsenious oxide. Hypochlorites also bleach vegetable colouring matters, but not after the addition of arsenious oxide. Chlorous acid is a very strongly oxidizing agent, and in this respect resembles chlorine dioxide; on the other hand, the chlorites—in alkaline soln.—do not exert so strong an oxidizing action. Iodides are oxidized to iodates: $3HClO_2+2KI=2KIO_3+3HCl$.

N. A. E. Millon[4] prepared soln. of potassium chlorite and sodium chlorite by adding chlorous acid slowly and gradually to a soln. of the alkali hydroxide until the product has a yellow colour. By rapidly evaporating the soln. to complete dryness, a deliquescent salt was obtained which, at 160°, decomposes into chlorate and chloride. This decomposition occurs if the soln. be slowly evaporated in vacuo. If an excess of chlorous acid is used with the potash-lye, a red liquid is obtained which gives off the acid on evaporation, and leaves a residue of the neutral salt. It has been suggested that the red liquid is a soln. of *acid potassium chlorite*.

K. G. Thurnlackh and K. F. von Hayn prepared a mixed soln. of potassium chlorate and chlorite by the action of potassium hydroxide free from chlorine on a soln. of chlorine dioxide. Light was carefully excluded, and the soln. was evaporated in vacuo at 45°–50°—potassium chlorate separated out first, and after further evaporation, alcohol was added, and the clear alcoholic soln. evaporated. Needle-like crystals of **potassium chlorite,** $KClO_2$, were obtained which deliquesced on exposure to air. As already indicated in connection with the preparation of the acid, G. Bruni and G. Levi made the potassium chlorite by reducing a soln. of potassium chlorate with oxalic acid; and A. Reychler, sodium chlorite, by the action of chlorine dioxide on a soln. of sodium peroxide. **Sodium chlorite,** $NaClO_2$, can be also made by double decomposition by treating a soln. of barium chlorite with sodium sulphate and evaporating the clear soln. in vacuo.

N. A. E. Millon found that a soln. of alkali chlorite gives a yellow precipitate of **lead chlorite,** $Pb(ClO_2)_2$, or of **silver chlorite,** $AgClO_2$, when treated respectively with lead or silver nitrate. On recrystallization from hot water, lead and silver chlorites are obtained in yellow plates. J. Schiel also made lead chlorite by treating a soln. of barium or calcium chlorite with lead nitrate; an excess of the lead nitrate is to be avoided because of its solvent action. Fine sulphur yellow crystals can be obtained from a warm soln.—50°–60°—of the salt in calcium chlorite. The dry salt explodes at 126° according to N. A. E. Millon, at 100° according to J. Schiel. It explodes when triturated with flowers of sulphur or antimony sulphide. It behaves like silver chlorite with hydrogen sulphide and with sulphuric acid.

If a trace of free chlorous acid is present with the precipitated silver chlorite,

N. A. E. Millon found that the chlorite decomposes readily into the chloride and chlorate: $3AgClO_2 = AgCl + 2AgClO_3$; and that the dried salt decomposes with detonation at 105°; when in contact with hydrochloric acid; or when rubbed up with flowers of sulphur. K. G. Thurnlackh and F. H. von Hayn say that the yellow colour of silver chlorite is bleached white in sunlight, but the salt is not decomposed by boiling water; it is rapidly reduced by sulphur dioxide; and when treated with sulphuric acid, a gas is evolved which has the colour and smell of chlorine dioxide. When hydrogen sulphide is passed over lead chlorite, black lead sulphide is first formed, and this oxidizes to white lead sulphate. J. Schiel seems to have obtained mixed crystals with lead chloride varying in composition between $6Pb(ClO_2)_2.4PbCl_2.PbO$ and $2Pb(ClO_2)_2.PbCl_2$. G. Bruni and G. Levi treated silver chlorite with conc. aqua ammonia, and obtained yellow crystals of **monammino-silver chlorite**, $AgClO_2.NH_3$; when a soln. of silver chlorite in ammoniated alcohol is treated with anhydrous ether, white crystals of the **diammino-silver chlorite**, $AgClO_2.2NH_3$, are obtained; and when dry gaseous ammonia is passed slowly over gaseous silver chlorite, a white crystalline precipitate, of the **triammino-silver chlorite**, $AgClO_2.3NH_3$, is formed. The two last-named ammino-salts are unstable in air, they lose ammonia, and become yellow. The three ammino-silver chlorites resemble the corresponding ammino-silver nitrites.

Calcium chlorite, $Ca(ClO_2)_2$; **strontium chlorite**, $Sr(ClO_2)_2$; **barium chlorite,** $Ba(ClO_2)_2$; and **lithium chlorite,** $LiClO_2$, were prepared by G. Bruni and G. Levi by the process previously indicated for barium chlorite. N. A. E. Millon made barium and strontium chlorites by the action of chlorous acid on the respective hydroxides as in the case of the alkali salts. Barium carbonate is not decomposed by the acid. N. A. E. Millon found the barium salt decomposed at 235°, and he added that the strontium salt decomposed less easily than the barium salt. The decomposition of barium chlorite in a bomb calorimeter gave $Ba(ClO_2)_2 = BaCl_2 + 2O_2 + 48.6$ Cals.; and hence follows $Ba + Cl_2 + 2O_2 = Ba(ClO_2)_{2solid} + 148.4$ Cals.; $BaCl_2 + O_2 = Ba(ClO_2)_2 - 48.6$ Cals.; $Ba(ClO_2)_2 + O_2 = Ba(ClO_3)_2 + 22.4$ Cals.; and $Ba(ClO_3)_2 + O_2 = Ba(ClO_4)_2 + 30.2$ Cals. Consequently, with compounds of chlorine in different degrees of oxidation, the heat of formation is less endothermic, *i.e.* more exothermic the higher the degree of oxidation. A. Angeli obtained an analogous result with the oxygenated nitrogen compounds.[5]

N. A. E. Millon sat. an aq. soln. of chlorous acid with ammonia. The soln. had bleaching qualities, and decomposed when evaporated. It is supposed to contain unstable **ammonium chlorite. Hydroxylamine chlorite** is unstable at ordinary temp.; it can be made like sodium chlorite, by treating barium chlorite with hydroxylamine sulphate. Mercuric chloride gives no precipitate with the chlorites. **Mercuric chlorite,** $Hg(ClO_2)_2$—possibly a basic chlorite, $3Hg(ClO_2)_2.HgO$—is prepared as a red crystalline precipitate by treating mercuric nitrate with barium or potassium chlorite, in not too dil. a soln. The dry salt is very unstable, and explodes spontaneously. **Mercurous chlorite,** $HgClO_2$, is obtained as a yellow crystalline salt by a method analogous to that used for the mercuric salt. The precipitate becomes white with an excess of the reagent; and the yellow salt reddens in air. The properties of the two mercury salts are similar in many respects.

Chlorites can be determined from the amount of ferrous iron oxidized to the ferric state: $4FeSO_4 + HClO_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + HCl + 2H_2O$. Neutral ferrous sulphate soln. give a brownish-yellow coloration with cold chlorite soln.; with hot soln., there is an ochreous deposit and an evolution of chlorine. When slightly acidulated, chlorites give a transient amethyst tint to a soln. of ferrous sulphate—*E. Lenssen's reaction*. Ferrocyanides are oxidized to ferricyanides. Potassium permanganate is decolorized, and a brown precipitate of hydrated manganese dioxide is formed. Brucine and diphenylamine give similar colorations with chlorites and chlorates; and the reagents for the nitrites give similar colorations with the chlorites. Solid chlorites deflagrate with sulphuric acid more energetically than do the chlorates. M. Brandau found that the chlorites, when heated, gave a

chloride and oxygen with the intermediate formation of a chlorite as well as chloride.

Bromous acid.—A. H. Richards[6] stated that while the addition of an excess of a cold aq. soln. of silver nitrate to bromine water produces hypobromous acid, on adding a large excess of bromine water to a soln. of silver nitrate, it is probable that the hypobromous acid, HOBr, first formed: $Br_2+AgNO_3+H_2O=HOBr+AgBr+HNO_3$, and the hypobromous acid is subsequently oxidized to bromous acid: $2AgNO_3+HOBr+Br_2+H_2O=HBrO_2+2AgBr+2HNO_3$. The excess of bromine can be removed by a stream of air; or by shaking with carbon disulphide. Analyses show that the ratio of the bromine to the oxygen in the solute is approximately as 1 : 2. The absence of hypobromous acid shows that the product is not a mixture of hypobromous and bromic acids. Attempts to make bromine trioxide, Br_2O_3, or *bromous anhydride*, have not been successful.

Iodine trioxide.—In 1859, T. Andrews and P. G. Tait[7] found that ozone immediately attacks iodine, forming a greyish-yellow powder, and the ozone is destroyed without change of volume. It has been stated that the powder is iodine monoxide, I_2O, but J. Ogier's analysis of the light yellow dust, obtained in small quantities by the action of a mixture of oxygen and ozone upon iodine vapour, corresponds with the formula I_2O_3. The powder is very deliquescent; it is decomposed by water, forming iodic acid and iodine, and by heat into iodine and oxygen, with a small residue of iodic acid. J. Ogier demonstrated the various stages in the oxidation of iodine by passing an electric discharge continuously through a tube containing oxygen and the vapour of iodine. In the lowest part of the tube is a layer of this oxide, and then follows iodine dioxide, IO_2 or I_2O_4; iodic anhydride, I_2O_5; and periodic anhydride, I_2O_7. P. Chrétien prepared yellow crystals of a compound to which he assigned the formula: $2SO_3.2I_2O_3.H_2O$, *i.e.* **basic iodine sulphate,** $(IO)_2SO_4.\frac{1}{2}H_2O$, by dissolving iodine in a hot soln. of iodic acid in sulphuric acid, or by heating a soln. of iodic acid in sulphuric acid to 250°–260°. The sulphate also crystallizes from a soln. of this oxide in cold conc. sulphuric acid. This substance is decomposed by water into iodine, iodic acid, and sulphuric acid. The action of water is taken to be $3I_2O_3+H_2O=2I_2O_5+2HI$; and $I_2O_5+10HI=6I_2+5H_2O$, so that the end products are $5I_2O_3=3I_2O_5+2I_2$. J. Ogier's oxide decomposes in a similar manner. F. Fichter and F. Rohner made a similar compound by treating a sat. soln. of iodine in chloroform with 8 per cent. ozone; and by treating powdered dry iodine with ozone at 40° to 50°; their analyses agree better with the formula I_4O_9 than with I_2O_3, I_2O_4, or I_3O_7, and they consider the compound to be an iodate of tervalent iodine, *viz.* **iodine iodate,** $I(IO_3)_3$, and represent the action of water to involve first the formation of iodic acid and iodine trihydroxide: $I(IO_3)_3+3H_2O=I(OH)_3+3HIO_3$, followed by the decomposition of the trihydroxide: $3I(OH)_3=2HIO_3+HI+3H_2O$; and iodine separates by the interaction of the iodic and hydriodic acids. F. Fichter and F. Rohner's oxide begins to lose iodine at 75°, and it decomposes vigorously at 120°–130°; it reacts violently with phenol, evolving the vapours of iodine.

H. Landolt assumes that **iodous acid,** HIO_2, is momentarily formed as an intermediate product in the reaction between iodic and sulphurous acids: $SO_2+HIO_3=SO_3+HIO_2$; followed by $SO_2+HIO_2=SO_3+HOI$; and by $SO_2+HOI=SO_3+HI$. According to E. Brunner, an iodite is always produced as a transient intermediate stage in the formation of iodates. Iodous acid has not been isolated, and its formation in these reactions is hypothetical. It is also very doubtful if the oxide formed by the oxidation of iodine with ozone can be regarded as the anhydride of iodous acid, HIO_2.

Several oxidized compounds of iodine have been reported at various times. No doubt many of them are mixtures of iodic or periodic acids or anhydrides with iodine, etc. For example, there is: (I) N. A. E. Millon's[8] *oxyde soushypoiodique*, $I_{10}O_{19}$, *i.e.* $I_2O_7.4I_2O_3$, formed as a yellow powder by the action of sulphuric acid on iodic acid. Millon regarded this oxide as hypoiodic anhydride, I_2O_4 or IO_2, mixed with a little iodous

anhydride, I_2O_3; but according to H. Keppeler, it is the basic iodine iodate, I_2O_4. (2) L. Sementini's product of the distillation of a mixture of iodine and potassium chlorate which F. Wöhler showed to be impure iodine chloride; and (3) Sementini's iodine oxide obtained by passing a mixture of iodine and oxygen through a red hot tube, or the distillation of a mixture of iodine and barium peroxide was shown by L. Gmelin [9] to be nothing but sublimed iodine. (4) E. Mitscherlich's oxide,[10] $(NaO)_2OI_2.10H_2O$, obtained by the spontaneous evaporation of a soln. of iodine in a soln. of sodium hydroxide or carbonate, and which, according to F. Penny, is probably a mixture of sodium iodide and iodate, NaI and $NaIO_3$. (5) A. Michael and W. T. Conn's product,[11] HI_7O_3, *i.e.* $HIO_3.(I_2)_3$, *obtained by the action of iodine on anhydrous perchloric acid.* This substance is hydroscopic and reacts with water, forming iodine and iodic acid: it is decomposed by heat into iodine and iodic acid. (6) H. Kämmerer's I_6O_{13} is formed as a brown powder [12] when iodine dioxide is left exposed to moist air. It is a mixture of iodine di- and pent-oxides. (7) Iodine reacts with ozone, forming a deliquescent oxide approximating in composition to I_4O_9, and is sometimes regarded as *iodine iodate*, $I(IO_3)_3$. This substance hydrolyzes in contact with water, forming iodic and hydriodic acids, and finally iodine and iodic acid: $5I_4O_9+9H_2O=18HIO_3+I_2$.

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§ 8. Chlorine Di- or Per-oxide.

In 1802, R. Chenevix obtained indications of the existence of a compound of oxygen and chlorine (oxymuriatic acid), in the yellow gas which he obtained by the action of sulphuric acid on potassium chlorate, and which he regarded *hyperoxygenized muriatic acid.* W. Cruickshank made a similar observation. In a paper [1] *On a combination of oxymuriatic acid and oxygen gas* (1811), H. Davy described a "peculiar gas" to which he gave the name euchlorine or euchloric gas—from εὖ, very; χλωρός, green—on account of its possessing a deeper yellowish-green colour than chlorine. This gas was prepared by gently warming a mixture of potassium chlorate with

an equal weight of hydrochloric acid diluted with its own weight of water. For a time the gas was supposed to be chlorine monoxide, and even chlorine trioxide, but E. Soubeiran showed that it is more likely to be a mixture than a definite compound because, when passed over mercurous chloride, chlorine is absorbed, and chlorine dioxide, discovered by H. Davy in 1815, remained. Mercury, copper, and antimony, which so readily burn in chlorine, are not acted upon by the cold gas; this might make it appear as if the gas does not contain free chlorine, but H. Davy also found that a mere mixture of chlorine dioxide and chlorine did not act immediately on copper leaf. In 1875, L. Pebal definitely proved that euchlorine is a mixture of chlorine dioxide with variable amounts of chlorine; and similar remarks apply to the *chlorochloric oxides*—Cl_6O_{13} and Cl_8O_{17}—of N. A. E. Millon (1843). In 1815, in an investigation: *On the action of acids on the salts usually called hyperoxymuriates, and on the gases produced from them*, H. Davy [2] announced the discovery of a gas now known as *chlorine dioxide* or *chlorine peroxide*—*chlorine tetroxide*, *Bioxyde de chlore*, *Chlordioxyd*, *Chlorperoxyd*, and formerly called *hypochloric acid*, or even *chlorous acid*. H. Davy made the gas in the following manner:

Powdered and dry potassium chlorate is rubbed with a small quantity of sulphuric acid, by means of a platinum spatula until the one was incorporated with the other, and a solid mass of a bright orange colour was formed. This mass was introduced into a small glass retort, and gently warmed by a water bath. A bright yellowish-green elastic fluid arose from the mixture, which was rapidly absorbed by water, giving to it its own tint, but which had no sensible action on mercury. To make the experiment without danger, not more than 3 to 4 grms. of potassium chlorate should be employed, and great care should be taken to prevent any combustible matter from being present, and the water-bath should not be permitted to attain a temp. equal to 100°.

A little while afterwards, F. von Stadion independently announced the discovery of the same gas. He said:

The rapidity with which sulphuric acid decomposes potassium chlorate is well known. If small quantities of the salt are treated with the acid, with the precaution of fusing the salt in the retort and, when cold, pouring sulphuric acid on the mass, the violence of the reaction is reduced, and, at a convenient temp., a gas is disengaged which can be collected over mercury, and which is designated *deutoxide of chlorine*. The residue in the retort contains potassium sulphate, and sparingly soluble unknown salt of a new acid (perchloric acid).

The preparation of chlorine dioxide.—In the reaction between sulphuric acid and potassium chlorate, it is assumed that chloric acid, $HClO_3$, is first formed: $KClO_3+H_2SO_4=KHSO_4+HClO_3$; and the chloric acid then decomposes into perchloric acid, $HClO_4$, and chlorine dioxide: $3HClO_3=HClO_4+2ClO_2+H_2O$. The purer and drier the chlorate the less the risk of explosion. All traces of organic matter must be excluded. The whole of the apparatus must be of glass—without rubber or cork stoppers or connections. The gas is more liable to explode in light than in darkness. N. A. E. Millon's directions [3] for preparing this explosive compound are:

About 100 grms. of sulphuric acid in a platinum dish are cooled by a freezing mixture of snow and salt. From 15 to 20 grms. of dry powdered potassium chlorate are added in small quantities at a time with a thorough stirring by means of a glass rod after each addition. The contents of the dish form a thick oily liquid which is poured through a long-stemmed funnel into a glass flask with a long drawn-out neck and of such a size that the flask is about one-third filled. The flask is well cooled, and great care is necessary to keep the neck of the retort free from the oily liquid. A piece of glass tubing of the same diameter as the drawn-out neck of the flask and fitting closely, glass to glass, is kept in place by rubber tubing. The flask is then placed in a water-bath and the temp. slowly raised to 20°; and later on to between 30° and 40°. The gas can be collected by the upward displacement of air in small dry flasks, or it can be liquefied by passing it through small U-tubes surrounded by a freezing mixture of snow and salt. The preparation is best conducted in a room illuminated by gas-light. Not more than 2 or 3 drops of the liquid should be collected in each U-tube. The gas contains some chlorine and oxygen as impurities.

V. A. Jacquelain heated a mixture of potassium chlorate and sulphuric acid diluted with its own volume of water in a long-necked flask in a water-bath at 70°. The flask was arranged so that half the neck was immersed in the water. A. Reychler has a safe method of preparing an aq. soln. of the gas by floating a dish containing potassium chlorate and dil. sulphuric acid, upon water in a larger dish, and covering the whole with a bell-jar. The water in the larger dish absorbs the chlorine peroxide as it is given off from the mixture in the smaller dish.

The gas can also be prepared by reducing potassium chlorate with oxalic acid,[4] or with vanadic acid.[5] According to W. Bray, a regular stream of chlorine dioxide is evolved without danger when a mixture of 40 grms. of powdered potassium chlorate, 150 grms. of crystallized oxalic acid, and 20 grms. of water is warmed in an oil bath to 60°.

The properties of chlorine dioxide.—Chlorine dioxide is a reddish-yellow gas with an unpleasant smell which produces headache; very dil. aq. soln. have a smell which is not unpleasant, and which has been likened to ozone. M. Faraday [6] liquefied the gas in 1823 and solidified it to an orange-red crystalline mass resembling potassium bichromate. The **melting point** of the crystals is −76°, and they freeze again at −79°. According to L. Pebal and G. Schacherl, the **boiling point** of the liquid is between 9° and 9·9° (731 mm.). If contact with organic matter is avoided, the liquid can be distilled. The **density** of the gas, air unity, is 2·330 according to L. Pebal, and 2·3984 at 11° according to G. Schacherl. The absorption spectrum of the gas, according to D. Gernez,[7] has lines in the blue and violet. G. D. Liveing and J. Dewar found nine shaded bands between 373 and 310$\mu\mu$, and some still feebler. The liquid absorbs the blue and violet completely; the gas is completely transparent in the ultra-violet.

The gas remains unchanged in darkness, but is gradually decomposed in **sunlight.** It detonates when rapidly heated to 100°; when subjected to electric sparks; or when shaken with mercury. Two volumes of the gas furnish one volume of chlorine and two volumes of oxygen: $2ClO_2=Cl_2+2O_2$. The aq. soln. is fairly stable in darkness; in sunlight, it decomposes rapidly in a few hours; and slowly in diffused daylight into chloric acid, $HClO_3$, chlorine, oxygen: $6ClO_2+2H_2O=Cl_2+O_2+4HClO_3$. Some perchloric acid is formed at the cost of the chloric acid: $2HClO_3+O_2=2HClO_4$. The presence of chlorides accelerate the rate of decomposition such that a soln. with 0·15 mol. of chlorine dioxide suffered a 2 per cent. decomposition in five weeks in darkness at 0°, while with a normal soln. of chloride, there was a 70 per cent. decomposition. In the presence of chlorides the reaction is represented: $6ClO_2+3H_2O=5HClO_3+HCl$; the velocity constants follow the relation $d[ClO_2]/dt=-K[ClO_2]^2[HCl]$, and accordingly it is inferred that there is a slow reaction: $2ClO_2+H_2O+HCl=2HClO_2+HOCl$, followed by a rapid change: $6HClO_2+3HOCl=5HClO_3+4HCl$. Platinized asbestos also accelerates the reaction like chlorides. In the presence of chlorine, the reaction progresses: $ClO_2+\frac{1}{2}Cl_2+H_2O=HClO_3+HCl$, with the side reactions: $6ClO_2+3H_2O=5HClO_3+HCl$, and $3Cl_2+3H_2O=HClO_3+5HCl$. At 60° another reaction: $ClO_2=\frac{1}{2}Cl_2+O_2$, sets in. Consequently, the decomposition of aq. soln. of chlorine dioxide is very complex, for there are (i) $2ClO_2=Cl_2+2O_2$, which is accelerated by raising the temp. or exposure to sunlight; (ii) $6ClO_2+3H_2O=5HClO_3+HCl$, which is accelerated by the presence of chlorides or by platinum; (iii) $2ClO_2+Cl_2+2H_2O=2HClO_3+2HCl$, which is accelerated by chlorine; (iv) $3Cl_2+3H_2O=HClO_3+5HCl$, which is accelerated by platinum or chlorine dioxide; and (v) $2Cl_2+2H_2O=4HCl+O_2$, which is accelerated by light. M. Blundell [8] found that a mixture of chlorine dioxide with $2\frac{2}{3}$ times its volume of **hydrogen** detonates when sparked, or exposed to the action of platinum sponge, and H. B. Dixon and E. J. Russell found the gas also explodes when mixed with **carbon monoxide.** According to H. B. Dixon and J. A. Harker, the **explosion wave** with a mixture of 53·6 per cent. of chlorine dioxide with 46·5 per cent. of oxygen is 1126 metres per second; and with 36 per cent. of oxygen, 1126 metres per second. **Mercury** slowly absorbs chlorine dioxide, forming

mercuric chloride, $HgCl_2$, and mercurous chlorate, $HgClO_3$. Chlorine peroxide is a powerful **oxidizing agent**—a piece of phosphorus, sulphur, sugar, or other combustible takes fire spontaneously in the gas, or produces an explosion.

Two well-known experiments may be cited to illustrate this. Place some crystals of potassium chlorate at the bottom of a test glass, and half fill the vessel with water. A few small pieces of yellow phosphorus are dropped into the glass, and conc. sulphuric acid is allowed to flow through a tube funnel on to the chlorate. The bubbles of chlorine peroxide which are evolved produced bright flashes of light when they come in contact with the phosphorus under the water. Again, powdered sugar and potassium chlorate are mixed with a feather on a sheet of paper and placed on a stone slab. When a drop of sulphuric acid is allowed to fall upon the mass, the chlorine peroxide which is formed ignites the sugar, and the flame rapidly spreads throughout the mass. Mixing the chlorate with turpentine, alcohol, ether, carbon disulphide, or fat oils gives similar results.[9]

The aq. soln. forms with **sulphur dioxide** two mols. of hydrochloric and five of sulphuric acid. **Sulphuric acid** at $-18°$ dissolves 20 volumes of chlorine dioxide, and is coloured yellow, any excess of chlorine dioxide is liquefied and floats on the soln. When the liquid is removed from the freezing mixture, it becomes red, and between $10°$ and $15°$ gives off chlorine and oxygen, and perchloric acid remains in the liquid. According to H. Kämmerer, **bromine** does not act on the gas or the aq. soln.; iodine behaves similarly with the gas, but there is a slight action with the aq. soln. **Iodine** separates from an acidified soln. of potassium iodide: $2ClO_2+10HI=2HCl+4H_2O+5I_2$; in neutral soln.: $6ClO_2+10KI=4KIO_3+6KCl+3I_2$; and in the bicarbonate soln.: $2ClO_2+2KI=2KClO_2+I_2$, whereby 80 per cent. of the chlorine dioxide is converted into the chlorite. With **ammonia,** the gas decomposes at ordinary temp. With the other **bases**—*e.g.* dil. potash lye—it forms a mixture of eq. parts of chlorite and chlorate, with conc. aq. soln. of the solid hydrate and conc. potash lye, an explosion may occur. A drop of solid potassium hydroxide causes liquid chlorine dioxide to explode. According to A. Reychler, equi-molecular quantities of chlorine dioxide and **potassium hydroxide** soln. react: $2ClO_2+2KOH=KClO_2+KClO_3+H_2O$, along with the side reactions: $2ClO_2=Cl_2+2O_2$, and $Cl_2+2KOH=KCl+KOCl+H_2O$. With an excess of potassium hydroxide the reaction is faster, with potassium acid carbonate, slower. With **sodium peroxide**, there is a very fast reaction: $Na_2O_2+2ClO_2=2NaClO_2+O_2$. According to E. Fürst, **potassium permanganate** is reduced and chloric acid is formed: $KMnO_4+3ClO_2+H_2O=MnO_2+KClO_3+2HClO_3$. The reaction with **nitrites** is not $2ClO_2+H_2O+5KNO_2=5KNO_3+2HCl$, as M. Brandau supposed, but rather, according to W. Bray, $2ClO_2+H_2O+KNO_2=KNO_3+2HClO_2$, which is shown to be a well-defined stage of the reaction if the soln. contains acid carbonates in which the chlorous acid is fairly stable. In acid soln., however, a yellow colour appears in consequence of the consecutive reaction: $HClO_2+2KNO_2=2KNO_3+HCl$. Some chlorous acid is also converted into chloric acid. Chlorine dioxide reacts with **zinc:** $Zn+2ClO_2=Zn(ClO_2)_2$; with **ferrous sulphate:** $2ClO_2+10FeSO_4+5H_2SO_4=2HCl+5Fe_2(SO_4)_3+4H_2O$. More chlorine dioxide is consumed than corresponds with this equation because some chloric acid is formed. Here probably chlorous acid $HClO_2$ is first formed, which subsequently decomposes into chloric and hydrochloric acids. With sodium **arsenite:** $2ClO_2+H_2O+5H_3AsO_3=5H_3AsO_4+2HCl$; this reaction is not quantitative since some chlorate is formed. Indigo, litmus, and other **organic colouring agents** are decolorized by chlorine dioxide. Chlorine dioxide dissolves in **water,** forming a dark green soln. Water at $4°$ dissolves 20 times its volume of gas. At low temp., N. A. E. Millon noticed the formation of a yellow hydrate which loses much gas during its melting. W. Bray prepared the hydrate by pouring the liquid dioxide into water at $0°$, and represented it as a **octohydrated chlorine dioxide:** $ClO_2.8H_2O(\pm H_2O)$. This hydrate decomposes at $18·2°$. The equilibrium conditions are illustrated by Fig. 7. The eutectic temp. between ice and the hydrate is $-0·79°$. The solubility of liquid chlorine dioxide below $18·2°$ is greater than that of the hydrate; at $18·2°$ the two solubilities

are the same, and at this quadruple point, liquid, hydrate, solution, and vapour are in equilibrium. At 18·2°, the hydrate is transformed into the liquid dioxide; below 18·2°, the hydrate is stable; above 18·2°, the liquid dioxide is stable—when the press. is enough to prevent the liquid boiling. The solubility of the liquid dioxide decreases with rise of temp., while the solubility of the hydrate increases. W. Bray obtained a white compound of the hydrate of chlorine dioxide analogous to one obtained by A. A. Jakowkin with chlorine. The partition coeff. of chlorine dioxide between carbon tetrachloride and water, C_{CCl_4}/C_{H_2O}, lies between 1·27 and 1·17 at 0°, and between 1·69 and 1·60 at 25°. The molecular state of the dioxide is the same in both liquids, and therefore chlorine dioxide is not hydrolyzed in aq. soln.

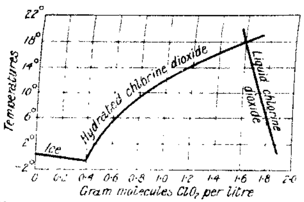

FIG. 7.—Equilibrium Conditions of Chlorine Dioxide and Water—W. Bray.

Composition.—H. Davy analyzed this gas by explosion over mercury, and although a little chlorine was absorbed by the mercury, he concluded that the gas is composed of two vols. of oxygen and one vol. of chlorine condensed into the space of two volumes. In symbols, $2ClO_2$ (2 vols.)$=Cl_2$ (1 vol.)$+2O_2$ (2 vols.). This conclusion was confirmed by J. L. Gay Lussac, who determined the composition of chlorine dioxide by passing the gas through a capillary tube with three bulbs of known capacity. The capillary tube was heated before the gas entered the bulbs. Decomposition took place in the capillary tube without explosion. The bulbs therefore contained the decomposition products of the chlorine dioxide—chlorine and oxygen. The chlorine was determined by absorption with potassium hydroxide and the oxygen in a gas-measuring tube. It was found that 100 volumes of the dioxide furnished 67·1 volumes of oxygen and 32·9 volumes of chlorine. Hence it was inferred that the simplest formula of chlorine dioxide is ClO_2. Further confirmation was obtained by L. Pebal, who heated the gas in a glass cylinder until it decomposed; the chlorine was determined by the potassium iodide process. The volume expansion on decomposition was 2 : 3·05; the ratio of the volume of chlorine to that of oxygen was 1 : 2·09; and the ratio of the volume of oxygen to the expansion 1·96 : 1. Thus, the chlorine in chlorine dioxide appears, at first sight, to be di- or quadrivalent. Chlorine in virtually all its other compounds has an odd valency. To overcome the difficulty, it was supposed that this formula must be doubled, and the formula was written Cl_2O_4 until L. Pebal and G. Schacherl had measured the vapour density of the gas and found it to be in harmony with the formula ClO_2. According to W. Bray, the mol. wt. of the gas in water, and in carbon tetrachloride, as solvents, agree with the formula ClO_2.

There is no evidence of the existence of *bromine dioxide* beyond H. Kämmerer's[10] unverified statement that in the distillation of 4 per cent. bromic acid, the distillate in some cases contains less oxygen than corresponds with bromic acid, and had the atomic ratio Br : O_2. If this be the case, the product soon decomposes into bromic acid and bromine or hydrogen bromide.

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§ 9. Iodine Di- or Tetra-oxide.

This product was prepared by N. A. E. Millon[1] in 1844, and later by H. Kämmerer by the partial reduction of iodic acid; and also by the incomplete oxidation of iodine with nitric acid. N. A. E. Millon called it *anhydride hypoiodique*, and by analysis he established its composition to be that represented by the formula IO_2 or I_2O_4. At present there is nothing to decide between these formulæ excepting a formal analogy with chlorine dioxide, ClO_2. F. Fichter and F. Rohner write the formula I_2O_4 and assume it is a basic iodine iodate, $O:I.IO_3$. The iodine oxides, $I_{10}O_{19}$ and I_6O_{13}, reported by N. A. E. Millon (1844) and by H. Kämmerer (1861), appear to be identical with basic iodine iodate, I_2O_4, or $IO(IO_3)$. The oxide, I_4O_9, was reported by F. Fichter and F. Rohner to be formed as a yellowish-white precipitate by the action of ozonized oxygen on a sat. soln. of iodine in chloroform, or by the action of ozone on powdered iodine at 40°–50°; it may be iodine iodate, $I(IO_3)_3$.

The preparation of iodine dioxide.—N. A. E. Millon's method of preparation by the reduction of iodic acid. modified by M. M. P. Muir, is as follows:

Heat in a platinum dish an intimate mixture of 60 grms. of powdered iodic acid and 200 grms. of conc. sulphuric acid. Stir the mass frequently. When oxygen has been evolved freely for a few minutes, and the mass is dark brownish-yellow, lower the flame, and stop the heating as soon as the violet vapour of iodine appears. Keep the dish over sulphuric acid for 4 or 5 days. Drain the liquid portion away from the yellow crystalline crust, and wash the powdered mass with a little of the liquid into a funnel fitted with a plug of glass wool, and drain the mass with the aid of the suction pump. Keep the solid on a dry porous tile in a desiccator for about a week; the solid is occasionally removed, rubbed to powder, and replaced on the tile. If a little of the solid, when shaken for a minute or two with a little cold water, loses no more than a trace of iodine, the yellow solid is transferred to another funnel fitted with a glass wool plug and a suction attachment, and washed by about five or six successive additions of small quantities of cold water until the washings are free from sulphates; then with small quantities of alcohol until the washings are colourless; and about three times with dry ether. The solid is kept on a porous tile in a desiccator over dry lime for a few days, and finally dried at 100°. A 30 per cent. yield on the iodic acid originally employed can be obtained.

According to N. A. E. Millon,[2] when dry finely powdered iodine is treated with ten times its weight of the most conc. nitric acid, a voluminous yellow powder is obtained which can be dried on a porous plate; it contains iodine, oxygen, and nitric acid, and was regarded as *nitroso-iodic acid*. If the iodine nitrate is treated with a current of dry carbon dioxide or air, or dried on a porous tile over lime so long as nitrogenous fumes are given off, it is decomposed into iodine dioxide and

nitrogen oxides. The iodic acid and iodine can be removed by washing with water and with alcohol.

H. Kämmerer supposed Millon's nitroso-iodic acid to be a nitroso-derivative of iodine pentoxide, *viz.* $I_2O_4(NO)_2$, but he gave no analyses in support of his hypothesis. H. Kappeler prepared Millon's nitroso-iodic acid, using nitric acid of sp. gr. 1·52; and his analyses fit the assumption that the formula of the compound corresponds with either **iodine nitrate,** $I(NO_3)_3$, or **basic iodine nitrate,** $IONO_3$—iodine tervalent. Consequently, in the oxidation of iodine, or in the reduction of iodic acid, when water is excluded as much as possible, the reaction ceases as soon as the tervalent iodine compound is produced. Thus, in the oxidation of iodine (i) with ozone—F. Fichter and F. Rohner's **iodine iodate,** $I(IO_3)_3$, is formed; (ii) with nitric acid—H. Kappeler's iodine nitrate, $I(NO_3)_3$, or $O:I.NO_3$, is formed; and in the reduction of iodic acid (i) with conc. sulphuric acid—P. Chrétien's basic **iodine sulphate,** $(IO)_2SO_4.\frac{1}{2}H_2O$, or (ii) with sulphur dioxide forming an **iodine sulphite** and sulphate. P. Chrétien has prepared a number of other crystalline sulphates—corresponding with $2SO_3.2H_2O.2I_2O_4$; $SO_3.H_2O.I_2O_4.10I_2O_5$; and $2SO_3.2H_2O.2I_2O_4.I_2O_5$. An **iodine acetate,** $I(C_2H_3O_2)_3$, was prepared by P. Schutzenberger, and H. Kappeler by the action of chlorine monoxide on a soln. of iodine in glacial acetic acid. If iodic acid be dissolved in a soln. of hydrofluoric acid in glacial acetic acid, and the soln. conc. by evaporation, colourless acicular crystals with a composition **iodine oxy-fluoride,** $IOF_3.5H_2O$, or $IF_3(OH)_2.4H_2O$, are obtained. The crystals give off fumes of hydrogen fluoride in moist air.

The properties of iodine dioxide.—Iodine dioxide is a lemon-yellow solid which separates from its soln. in hot conc. sulphuric acid in minute crystals which are not hygroscopic. The salt prepared by F. Fichter and F. Rohner deliquesced in air, forming a black syrup; iodine vapours were slowly evolved, and crystals of iodic acid remained. The compound decomposed slowly at 75°, and rapidly at 120°–130°. The specific gravity at 10° is 4·2 (water at 10° unity). Iodine dioxide reacts slowly with cold **water** and quickly with hot water to produce iodine and iodic acid: $5I_2O_4+4H_2O=8HIO_3+I_2$; it is insoluble, and is not acted upon by dry **ether** or glacial **acetic acid,** and it dissolves very slowly and slightly in **acetone** and **monochloracetic acid.** It reacts with an aq. soln. of **oxalic acid,** $H_2C_2O_4$, in the presence of sulphuric acid at 100°, forming iodine, water, and carbon dioxide: $I_2O_4+4H_2C_2O_4=I_2+4H_2O+8CO_2$. It reacts very slowly with **alcohol,** forming iodine pentoxide, and iodine passes into soln. Cold **nitric acid,** dil. or conc., converts iodine dioxide into iodine and iodic acid; cold conc. **hydrochloric acid** forms a yellow soln. which gives off chlorine; no iodine is separated, and the soln. probably contains iodic acid and iodine chloride, but, after boiling, the iodic acid is all decomposed. Cold dil. **sulphuric acid** acts slowly on iodine dioxide, forming iodine and iodic acid; boiling dil. sulphuric gives the same result as boiling water. Cold 99 per cent. sulphuric acid dissolves the compound slowly—at 15°–20°, 100 c.c. of the acid dissolve 1·54 grms. of iodine dioxide; sulphuric acid, $H_2SO_4.H_2O$, dissolves iodine dioxide more freely than the 99 per cent. acid. The soln. in conc. sulphuric acid deposits crystals of what has been called *Millon's sulphate,* which F. Fichter and F. Rohner consider to be a mixture of iodine pentoxide and $I_2O_3.SO_3.\frac{1}{2}H_2O$. When the soln. with fuming sulphuric acid is heated, it becomes green and then yellow—no iodine is given off, but a yellow solid (93 per cent. iodine dioxide with some pentoxide) is deposited on cooling. There is no evidence of the formation of a compound of iodine dioxide and sulphuric acid, but if iodine dioxide be sat. with the fumes of **sulphur trioxide** and then kept in a desiccator for some days, a compound $I_2O_4.3SO_3$ is formed.

This product is a pale yellow hygroscopic solid, which can be kept unchanged for months. It gives off oxygen, iodine, and sulphur trioxide at about 120°, but at 190° the residue still retains some sulphur trioxide. The compound $I_2O_4.3SO_3$ dissolves in a large quantity of water with decomposition, forming iodine, iodic and sulphuric acids. It forms a yellow soln. in well-cooled alcohol, and the alcoholic soln. on evaporation at

ordinary temp. gives crystals of iodic acid. Ether removes the sulphur trioxide and leaves iodine dioxide behind.

H. Kappeler made a similar sulphate by reducing solid iodic acid with dry **sulphur dioxide.** Aq. potassium hydroxide reacts with iodine dioxide to form potassium iodate and iodide: $6IO_2+6KOH=5KIO_3+KI+3H_2O$. The oxide I_4O_9 is thought to be iodine iodate, with tervalent iodine, namely, $I(IO_3)_3$, for it reacts with water, forming what is thought to be *iodine hydroxide*, $I(OH)_3$, and iodic acid: $I(IO_3)_3+3H_2O=3HIO_3+I(OH)_3$; the iodine hydroxide then breaks down by a slow reaction into iodic and hydriodic acids: $3I(OH)_3=2HIO_3+HI+3H_2O$, and these acids then react with the liberation of iodine—*vide supra*. The salts of iodine are also hydrolyzed by water, forming iodine iodate, which in turn is decomposed as just indicated. The reactions are very slow, so that the iodic acid formed may have time to react with the undecomposed salt, forming a basic iodine iodate, $IO(IO_3)$, thus: $(IO_2)SO_4+2HIO_3=2(IO_3)IO_3+H_2SO_4$; with iodine acetate, however, the decomposition by water is too fast to permit the formation of basic iodine iodate in this manner.

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§ 10. The Halogen Pentoxides

Neither bromine nor chlorine pentoxide is known, but iodine pentoxide is a relatively stable compound. This is in agreement with the estimated heats of formation: $Cl_2O_{5aq.}$ −20·5 Cals.; $Br_2O_{5aq.}$ −43·3 Cals.; $I_2O_{5aq.}$ +43·75 Cals. Hence, while the two first-named oxides are strongly endothermal, the last-named oxide is strongly exothermal. Iodine pentoxide was almost simultaneously and independently made by J. L. Gay Lussac [1] and H. Davy in 1813. H. Davy made this binary compound by oxidizing iodine with euchlorine dried by muriate of lime. The iodine assumes a bright orange coloration, and, by the application of a gentle heat, iodine chloride is volatilized, and there remains a compound of iodine and oxygen which he called *oxyiodine*. The acid which oxyiodine forms with water was called *oxiodic acid*. These names are now changed to iodine pentoxide and iodic acid respectively. Iodine pentoxide, I_2O_5, is also called iodic anhydride because it reacts with water to form iodic acid.

The preparation of iodine pentoxide.—Iodine pentoxide is formed by oxidizing iodine, or by dehydrating iodic or periodic acids. J. Ogier formed small quantities of this oxide by oxidizing iodine vapour mixed with oxygen exposed to a silent electrical discharge; it is also formed when ozone is led into a soln. of potassium iodide; and, according to G. Salet, when iodine is passed through the hydrogen flame, iodine pentoxide is one of the products of combustion.

H. Basset and E. Fielding [2] formed iodine pentoxide by the oxidizing action of gaseous chlorine monoxide, or of a soln. of chlorine monoxide in carbon tetrachloride, upon iodine chlorine: $5Cl_2O+2ICl_3=I_2O_5+8Cl_2$; A. Michael and W. T. Conn formed the same oxide by oxidizing iodine with chlorine heptoxide, Cl_2O_7; the resulting white powder decomposes into iodine pentoxide at about 110°. M. Guichard obtained a 40 per cent. yield by wetting iodine with fuming nitric acid, and spreading it in a tube through which nitric anhydride is passed.

Iodine pentoxide, however, is most conveniently prepared by the dehydration

of iodic acid at comparatively low temp. There is no sign of any sublimation even when the heat is carried to the point of decomposition. The water of composition may be driven from the iodic acid without fusion. G. P. Baxter and G. S. Tilley found that if the powdered iodic acid be heated slowly at 110°, all the water may be expelled if the time of heating be prolonged. If the acid be rapidly heated, it melts at 110° with the separation of a solid phase, $I_2O_5.HIO_3$, which shows no indications of melting up to about 250° though it still contains up to 0·006 per cent. of moisture.

The material is best heated in a tube between 90° and 110° so that the first portion of the water may be expelled without fusion. The temp. is then raised to 220°, and the operation concluded by a 4 hrs. heating at 240°, dry and purified air is passed through the tube during the operation. If fusion occurs before dehydration, some iodic acid may be enclosed within an impervious coating of anhydrous salt, and the escape of water prevented.[3] If the air is inadequately dried, the iodine pentoxide may become brown, probably owing to the liberation of iodine; and a similar result is obtained when the temp. rises over 250°.

N. A. E. Millon and C. Rammelsberg[4] made iodine pentoxide by dehydrating iodic acid with sulphuric acid at about 170°. P. Chrétien found that sulphuric acid dissolves about one-fifth of its weight of iodic acid at 200°, but oxygen is always evolved, showing that some decomposition occurs at this temp. If the soln. be poured into a porcelain crucible containing a little fuming nitric acid, colourless crystals of iodine pentoxide are formed. The crystals contain 2 to 3 per cent. of sulphuric acid; most of this can be removed by finely powdering the crystals and redrying them on porous tiles. C. F. Rammelsberg also prepared iodine pentoxide by the action of sulphuric acid on barium iodate, which M. Guichard found gave an impure product on account of the solubility of barium sulphate in iodic acid. The material can be purified by adding the aq. soln. to nitric acid of specific gravity 1·33, and concentrating until iodic acid separates. H. Lescœur and M. Nicloux dehydrated iodic acid by heating it to 170° with conc. or fuming nitric acid. A. B. Lamb also prepared iodine pentoxide by dehydrating periodic acid at 110°.

The properties of iodine pentoxide.—Iodine pentoxide is a white powder which C. F. Rammelsberg[5] says consists of crystals which have a sharp acid taste. According to A. Ditte, the sp. gr. at 0° is 5·037 and at 51°, 5·020; H. Kämmerer gave 4·799 at 9°; G. P. Baxter and G. S. Tilley at 25° gave 4·799. The coeff. of expansion is 0·000066 between 0° and 51°. The heat of formation $2I_{solid}+5O=I_2O_5+45029$ cals. at 13° (J. Thomsen), 48000 cals. (M. Berthelot); $2I_{solid}+5O+_{aq.}=I_2O_{5aq.}$ $+43240$ cals. at 13° (J. Thomsen), 46400 cals. (M. Berthelot). The high heat of formation is in accord with the relative stability of the pentoxide. The molecular heat of soln. is −1792 cals. at 17° (J. Thomsen); −1620 cals. at 12° (M. Berthelot).

At ordinary temp., iodine pentoxide is decomposed by exposure to sunlight as is evident by its colour; similar remarks apply to radium radiations[6]—these reactions are endothermal. Iodine decomposes slightly when heated to about 250° in vacuo; and it decomposes quickly between 300° and 350°, and acquires a brown colour. According to M. Guichard, the brown colour is not removed by extracting the solid with carbon disulphide, benzene, ether, or fuming nitric acid. The conditions for the reversible reaction: $2I_2+5O_2 \rightleftharpoons 2I_2O_{5solid}$, are difficult to find, since there are no signs of a reaction between iodine and oxygen at 360° and 35 atm. press.; and the compound is completely decomposed at 370° with a press. of 200 atm. According to M. Berthelot, no signs of combination are perceptible at 500° or at a higher temp., and according to K. Wehsarg, the two elements do not unite in the presence of platinum sponge or platinized asbestos. According to A. Connell, when an electric current is sent through the molten compound, decomposition occurs, but it is not clear if this is but a thermal effect.

According to A. Ditte,[7] the iodine pentoxide which has separated from an acid soln. slowly loses some water at 180°, and rapidly if the powdered substance is heated to 200°–210°, and even after heating to 250°, it may contain up to 0·006 per cent.

of moisture. The oxide is deliquescent in moist air, and dissolves in water to form iodic acid: $I_2O_5+H_2O=2HIO_3$. According to H. Kämmerer, a gram of water at 13° dissolves 1·874 grms. of iodine pentoxide—*i.e.* water dissolves nearly twice its weight of the solid. It is insoluble in ether, carbon disulphide, chloroform, and the volatile hydrocarbons.

In virtue of the facility with which it decomposes into iodine and oxygen, iodine pentoxide is a strong oxidizing agent. The behaviour of this oxide towards the different elements and compounds has been investigated by A. Ditte. As shown by H. Davy, iodine pentoxide reacts explosively when warmed with **carbon, sulphur,** sugar, resin, and powdered easily combustible elements. It does not react with **hydrogen** at ordinary press. cold nor at its decomposition temp. 300°, but in a sealed tube at 250°, it forms water and iodine vapour; the same result is obtained in the presence of platinum sponge at ordinary temp. **Chlorine** and **bromine** have no action; dry **hydrogen chloride** at ordinary temp. reacts with the development of heat, forming iodine chloride and chlorine. **Cyanogen** forms oxygen and iodine cyanide, ICy, and the resulting mixture of cyanogen and oxygen detonates. Iodine pentoxide does not react with **carbon monoxide** at ordinary temp., but A. Ditte found that if warmed carbon dioxide and iodine are formed: $5CO+I_2O_5=5CO_2+I_2$, and on this reaction A. Gautier has based a method for the determination of carbon monoxide from the amount of iodine set free.[8] The reaction is said to be sensitive to the presence of carbon monoxide dil. with 30,000 times its volume of air. If acetylene be present, it reacts: $C_2H_2+I_2O_5=I_2+2CO_2+H_2O$. Gaseous **nitric oxide,** NO, does not react at ordinary temp., but a soln. of this gas in conc. sulphuric acid reacts slowly at 100°. **Ammonia** has no action at ordinary temp., but when warmed the reaction is symbolized: $3I_2O_5+10NH_3=5N_2+3I_2+15H_2O$. **Hydrogen sulphide** when warmed with iodine pentoxide forms water, iodine, hydrogen iodide, and sulphur. When warmed with **sulphur dioxide** it forms sulphur trioxide. According to H. Kämmerer, if the reacting substances are quite dry, a compound corresponding with $5I_2O_5.SO_3$ is formed with the loss of iodine, which rapidly absorbs moisture from the air, and is decomposed by **water** or aq. **alkali hydroxide** —but not with alcohol, ether, or alcoholic potash—with the separation of iodine, and the formation of a residual product, I_6O_{13}, which he thinks is either $2I_2O_4.I_2O_5$, or $2I_2O_3.I_2O_7$. A. Ditte denies the existence of this compound, and considers that iodine and sulphuric acid are formed by the action of sulphur dioxide on iodine pentoxide. When dissolved in sulphuric acid, iodine pentoxide is not attacked by sulphur dioxide in the cold or at 100°. In addition to H. Kämmerer's [9] $5I_2O_5.SO_3$, R. Weber has described a compound $I_2O_5.3SO_3$, and M. M. P. Muir a compound $I_2O_5.2SO_3$, formed by the action of iodine pentoxide on **sulphur trioxide** in a sealed tube at 100°.

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§ 11. The Preparation of Chloric, Bromic, and Iodic Acids, and of their Salts

About the middle of the seventeenth century, 1658, J. R. Glauber[1] described the conversion of hydrochloric into nitric acid, and mentioned the preparation of saltpetre from common salt. J. J. Winterl (1789) also thought that he had transformed hydrochloric into nitric acid by passing the gas obtained by heating calcium chloride with pyrolusite—probably chlorine—into potash lye. The salt which crystallized out from the lye was thought to be nitre. In all these cases, H. Kopp considers that potassium chlorate was formed and mistaken for potassium nitrate. After the discovery of chlorine, C. W. Scheele, in 1774, noted that it forms with the fixed alkalies—potash and soda—a kind of *sel marin* which decrepitates on hot charcoal but does not detonate. T. Bergmann (1778) said that this gas forms the same salt as hydrochloric acid does with the alkalies and earths, and explained C. W. Scheele's observation in terms of the phlogiston theory; but B. Higgins (1786) showed that under these conditions chlorine produces a kind of saltpetre which C. L. Berthollet independently obtained in crystalline plates about the same time. Berthollet said:

> When alkali lye is treated with chlorine—*l'acide muriatique oxigéné*—so that the alkali is maintained in excess, the liquid readily destroys vegetable colours; but with the chlorine in excess, the *sel oxigéné* which is produced exercises no action on these colours.

He called the new salt *muriate oxigéné de potasse*. At the beginning of the nineteenth century, Berthollet's new compounds were called *muriates oxigénés* or *muriates suroxigénés*; to-day they are designated *chlorates*. C. L. Berthollet showed that the new *sel oxigéné* must be regarded as a compound containing more oxygen than chlorine—*acide muriatique oxigéné*—and he called the new acid *acide muriatique suroxigéné*. C. L. Berthelot said:

> The acid which forms the *sels oxigénés* must be different from those formed by oxygenated muriatic acid (chlorine) in composition and properties; but up to the present time, I have not been able to obtain the new acid free from the base, without a partial decomposition, so that I have not observed it in a free state.

The salt was investigated by R. Chenevix in 1802; and in 1814, J. L. Gay Lussac obtained an aq. soln. of the new acid—chloric acid. He said:

> I prepared a quantity of *muriate suroxygéné de baryte* (barium chlorate), and treated a dil. soln. of this salt with dil. sulphuric acid, taking care to add no more acid than is needed to sat. the baryte. . . . In this way, I prepared a soln. of the acid quite free from sulphuric acid and from baryta. The soln. gave no precipitate with silver nitrate; it contained *l'acide chlorique* in aq. soln.

Bromic acid was discovered by A. J. Balard [2] in 1826 and described in his classical memoir, *Sur une substance particulière contenue dans l'eau de la mer*; A. J. Balard was of course guided in this work by the analogy which he found between bromine and iodine. Iodic acid was discovered by J. L. Gay Lussac and H. Davy [3] in 1813; and, in 1831, A. Connell obtained it by the direct oxidation of iodine by nitric acid.

The preparation of alkali chlorates.—J. L. Gay Lussac [4] showed that when chlorine is passed into a cold soln. of potassium hydroxide, a mixture of potassium chloride and hypochlorite is formed; and when the soln. is boiled the hypochlorite decomposes, forming a mixture of potassium chlorate and chloride; otherwise expressed, the hypochlorite in soln. oxidizes itself: $3KOCl=2KCl+KClO_3$. This reaction occurs with the evolution of 23·8 Cals. of heat. The conversion of hypochlorites to chlorates is hastened when an excess of chlorine is employed. The excess of chlorine converts some of the hypochlorite into free hypochlorous acid, and this condition is eminently favourable to the formation of chloric acid: $2HOCl+KOCl=KClO_3+2HCl$. The freed hydrochloric acid then liberates an eq. amount of hypochlorous acid: $HCl+KOCl=KCl+HOCl$, and the hypochlorous acid oxidizes more hypochlorite. So the process continues until all the hypochlorite is transformed to chlorate. A slight acidity, therefore, accelerates the formation of the chlorate. F. Winteler has shown that the yield of chlorate is greatly influenced by the conc. of the alkali lye. There is a certain conc. for which the yield of chlorate is a maximum; any further increase in the conc. of the lye results in a diminished yield of chlorate, for the products of the reaction break down, yielding oxygen and the corresponding chloride. This is illustrated by the curve, Fig. 8, which shows the yield of chlorate obtained when hot sodium hydroxide soln. containing one per cent. of hypochlorite are heated to 100° for half an hour. According to F. Winteler, the speed of decomposition of bleaching powder into chloride and oxygen is accelerated by soluble hydroxides, and this the more, the greater the concentration of the latter. This is illustrated by the curve, Fig. 9, which shows the effect of treating soln. of bleaching powder under similar conditions at 100° with gradually increasing amounts of alkali. The ordinates represent the amount of undecomposed chlorate at the end of half an hour.

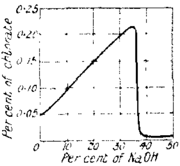

FIG. 8.—The Effect of Sodium Hydroxide on the yield of Chlorate.

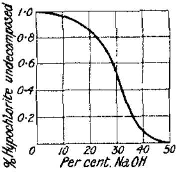

FIG. 9.—The Influence of Alkali on the Decomposition of Hypochlorite.

The conversion into chlorate is hastened by raising the temp., and therefore chlorine is passed into a *hot* (70°) aq. soln. of potassium hydroxide: $6KOH+3Cl_2=KClO_3+5KCl+3H_2O$; and the two salts—potassium chloride and potassium chlorate—can be separated by fractional crystallization, since potassium chlorate is far less soluble than the corresponding chloride. A soln. of potassium carbonate can be used in place of a soln. of potassium hydroxide, but there is then a greater loss of chlorine and hypochlorous acid. According to A. Morin, the escape of oxygen during the evaporation of the soln. of chlorine in alkali hydroxide reduces the yield so much that only one-nineteenth instead of one-sixth of the potassium is obtained as chlorate, the remainder is the less valuable chloride. This loss is serious, because potassium hydroxide is relatively expensive. This fact, coupled with the comparatively difficult separation, renders J. L. Gay Lussac's method of small technical interest. T. Graham suggested saving potash by saturating an intimate mixture of eq. proportions of potassium carbonate and slaked lime, and after heating the mass to decompose the hypochlorites, extracting the residue with

water. Potassium chloride and chlorate dissolved; calcium carbonate remained behind. F. C. Calvert similarly passed chlorine into a heated mixture of potash lye and lime. J. von Liebig evaporated to dryness a mixture of water and bleaching powder. The mass was extracted with water, and the resulting soln. of calcium chloride and chlorate was treated with the necessary amount of potassium chloride and evaporated. There is a serious loss of oxygen during evaporation. The only satisfactory technical process, apart from electrolysis, is also based on a later suggestion of J. von Liebig, who showed that it is cheaper to substitute a hot soln. of slaked lime in water for the potassium hydroxide soln. In that case: $6Ca(OH)_2+6Cl_2=Ca(ClO_3)_2+5CaCl_2+6H_2O$. As in the case of potassium hydroxide, the action of chlorine on the lime liquor is to form the chloride and hypochlorite: $2Ca(OH)_2+2Cl_2=2H_2O+CaCl_2+Ca(OCl)_2$; this is followed by two reactions: (i) the conversion of hypochlorite into the chlorate by heat: $3Ca(OCl)_2=Ca(ClO_3)_2+2CaCl_2$; and (ii) the conversion of hypochlorite into chlorate by the action of an excess of chlorine: $3Ca(OCl)_2=2CaCl_2+Ca(ClO_3)_2$, probably through the intermediate formation of hypochlorous acid: $Ca(OCl)_2+2Cl_2+2H_2O=CaCl_2+4HOCl$; followed by $Ca(OCl)_2+4HOCl=Ca(ClO_3)_2+4HCl$. The hydrochloric acid then liberates more hypochlorous acid: $Ca(OCl)_2+2HCl=2HOCl+CaCl_2$, and so, in a continuous cycle of operations, until all the hypochlorite is converted into chlorate.[5] These reactions are accelerated by raising the temp. G. Lunge and L. Landolt found that merely raising the temp. of a soln. of chloride of lime is not very effective in transforming hypochlorite to chlorate—the transformation after 3 hrs. heating at 60° is hardly perceptible; the conversion is appreciable after further heating to 70° for an hour; and more so after another 2 hrs. heating to 90°; but even after boiling another 2 hrs., not much more than 25 per cent. of the chlorine had been utilized in the production of chlorates. If the chlorine be in excess the case is different: 70 per cent. was converted into chlorate at 15°; and but little more was converted after standing some time, or on warming up to 40°. The conversion was complete on boiling the soln. The excess of chlorine also prevented the loss of oxygen observed when alkaline soln. are boiled. Consequently, the most favourable conditions for the conversion of the hypochlorite into chlorate involve both the raising of the temp. and the use of an excess of chlorine. The clear soln. of calcium chlorate and chloride is conc. a little by evaporation, and a slight excess of potassium chloride is added. The potassium chlorate which is formed has but one-tenth the solubility of the corresponding calcium chlorate and is far less soluble than the other two chlorides; hence, by a further conc. of the soln., the least soluble potassium chlorate separates: $Ca(ClO_3)_2+2KCl=2KClO_3+CaCl_2$. The potassium chlorate so obtained is purified by recrystallization. W. Weldon (1871)[6] proposed to substitute magnesia for lime; T. Twyman, dolomite; and K. J. Bayer, zinc oxide.[7] These suggestions have not been industrially successful, and potassium chlorate prepared by the zinc process may be contaminated with zinc.

The electrolytic process for alkali chlorate.—The old process of J. von Liebig is now almost superseded by the electrolytic process; indeed, after the introduction of the electrolytic process, the price of the chlorate soon fell from £60 to £35 per ton, and abundantly justified H. Davy's prediction (1806): "It is not improbable that the electric decomposition of neutral salts, in different cases, may admit of economical uses." When hot soln. of potassium chloride are electrolyzed, the initial and end stages of the reactions are represented: $KCl+3H_2O=KClO_3+3H_2$; but no doubt chlorine is first formed; then potassium hypochlorite; and finally potassium chlorate and chloride. The sparingly soluble potassium chlorate crystallizes from the soln. during the electrolysis, and thus gives trouble. Since 100 c.c. of water at 20° dissolve about 99 grms. of sodium chlorate, and 100 c.c. of water about 7·2 grms. of potassium chlorate, it is best to prepare first sodium chlorate by the electrolysis of sodium chloride; and then treat the soln. with potassium chloride as in the case of calcium chlorate described above. Potassium chlorate can be isolated by fractional crystallization.

During the electrolysis of a soln. of an alkali chloride, the primary products are chlorine and alkali hydroxide; alkali hypochlorite then appears together with a little free hypochlorous acid as a result of the hydrolysis of the alkali hypochlorite. The alkali chlorate is then formed in two ways: (i) chemically—by the oxidation of the alkali hypochlorite by the hypochlorous acid: $NaOCl+2HOCl \rightleftharpoons NaClO_3+2HCl$; and (ii) electrochemically—by the oxidation of the hypochlorite by the oxygen developed at the anode; the former reaction is slow, and the latter gives a maximum efficiency of 66 per cent.[8] The presence of free alkali diminishes the hydrolysis and enables the chlorate formation, and the evolution of oxygen, to commence sooner, and with a lower concentration of hypochlorite than in a neutral soln. This phenomenon is the more pronounced the greater the alkalinity of the soln. until a maximum chlorate production is attained, as illustrated by the graph, Fig. 9. If the alkalinity of the soln. increases beyond this point, the discharge of oxygen increases, and the rate of formation of the chlorate diminishes. A low anode potential favours the evolution of oxygen, and diminishes the yield of chlorate; but a larger concentration of hypochlorite is needed for a discharge at a low polarization. Hence, better chlorate yields, and lower hypochlorite concentrations are attained with polished than with platinized platinum electrode. A rise of temp. increases the concentration of the hypochlorite and decreases the yield of chlorate. With acidified soln. of the alkali chloride, the concentration of the free acid is increased, and this favours the reaction: $2HOCl+NaOCl=2HCl+NaClO_3$. Although this reaction is slow at ordinary temp., its velocity is very much augmented at, say, 70°; and under this condition this reaction plays the larger part in the production of chlorate. If cathodic reduction is avoided by the use of a chromate, and no hypochlorite ions are discharged, a 100 per cent. current efficiency would be possible since no oxygen is discharged from the system. According to F. Förster and E. Müller, the conditions favourable to the formation of chlorate are (i) the use of a slightly acid electrolyte; (ii) the provision of means for preventing cathodic reduction; and (iii) the maintenance of the temp. above 40° to prevent the formation of perchlorates.

There are two types of process for the technical production of chlorates. In one, alkaline electrolytes are used with a possible 100 per cent. efficiency. The alkaline process, typified by that of F. Oettel,[9] has given place to the acidic process on account of the higher electrochemical efficiency of the acidic process. The first electrolytic chlorate processes—F. Hurter, and H. Gall and A. de Montlaur (1884)—used neutral soln. with diaphragm cells. The electrolyte was circulated from cathode to anode to avoid the reduction of the chlorate—the current efficiency was about 25 per cent. The use of chromate, etc., for avoiding cathode reduction has led to the disuse of diaphragm cells. In A. E. Gibbs's and P. L. E. Lederlin and P. E. C. Corbin's processes, the hot brine—about 25 per cent. concentration between 60° and 70°—flows through a series of compartments between the electrodes, where it is converted to chlorate, and the liquor containing unchanged brine and up to about 30 per cent. of chlorate escapes from the cell. The chlorate is crystallized out, and the unchanged liquor is run back into the electrolyzer. The loss of chlorate by the reducing action of the hydrogen at the cathode has been the subject of several patents: The use of about 0·2 per cent. of calcium chloride; potassium dichromate and hydrochloric acid; aluminous salts, clay, or silicic acid; fluorides; vanadium salts; etc., has been suggested in order to raise the yield of chlorate by preventing cathodic reduction—probably by forming a thin inert layer on the cathode which acts as a kind of diaphragm, preventing the evolved hydrogen from coming readily into contact with the hypochlorite in soln.

The preparation of chloric acid.—J. L. Gay Lussac[10] prepared a soln. of chloric acid by treating barium chlorate with the proper quantity of sulphuric acid.

V. Bernard dissolved 800 grms. of barium chlorate in 1700 c.c. of distilled water, and added 343 grms. of 52·4 per cent. sulphuric acid in small quantities at a time. The temp.

was kept low to avoid the formation of perchloric acid. The filtered soln. of chloric acid was colourless and contained only a trace of sulphuric acid ; it possessed a sp. gr. of 1·11 *at 20°.*

G. S. Sérullas treated potassium chlorate with an excess of hydrofluosilicic acid ; the clear liquid was decanted from the sparingly soluble potassium fluosilicate, the soln. evaporated below 30°, and filtered through glass powder ; J. J. Berzelius evaporated the acid liquid mixed with finely divided silica below 30° in air, or over conc. sulphuric acid and potassium hydroxide in vacuo. The excess of hydrofluoric acid was volatilized as silicon fluoride, and the clear liquid was then filtered from the excess of silica. R. Böttger treated sodium chlorate with oxalic acid whereby sparingly soluble sodium oxalate was formed ; J. L. Wheeler, and T. B. Munroe treated sodium chlorate with hydrofluosilicic acid ; and M. Brandau treated potassium chlorate with aluminium sulphate and sulphuric acid and precipitated the alum so formed with alcohol. Chloric acid is formed in many reactions with hypochlorous and chlorous acid ; for example, it is formed when an aq. soln. of chlorine or hypochlorous or chlorous acid decomposes in light. It is also formed when an aq. soln. of chlorine dioxide stands in darkness or in light. A mixture of alkali chlorate and chlorite is formed when an aq. soln. of an alkali hydroxide is treated with chlorine dioxide.

E. Fürst[11] found that a chlorate is formed when potassium permanganate is treated with chlorine dioxide ; and G. Gore obtained silver chlorate by treating a soln. of silver fluoride with chlorine : $6AgF+3H_2O+3Cl_2=AgClO_3+5AgCl+6HF$ —some oxygen is formed at the same time. H. Kämmerer found that some ammonium chlorate is produced when iodic acid is warmed with a soln. of silver chloride in an excess of ammonia.

J. Sand[12] attempted to calculate the equilibrium constant of the reaction $3H_2O+3Cl_2=HClO_3+5HCl$ on the assumption that the velocity of the reverse reaction is $dx/dt=k(ClO'_3)(Cl')^2(H^\cdot)^2$ but R. Luther and F. H. MacDougall showed that it is $dx/dt=k(ClO'_3)^2(H^\cdot)^4$. A. Skrabel calculated the constants for the analogous bromine and chlorine reactions. The reaction is very slow at ordinary temp., and by raising the temp. the slow consecutive reaction $2HClO_3=2HCl+3O_2$ is also accelerated. A. R. Olson worked at 91° and measured the constant directly. He found $k=(H^\cdot)^2(Cl')^5(ClO'_3)/(Cl)_3=4{\cdot}3\times10^{-7}$.

The preparation of bromic acid and the bromates.—Like chloric acid, free bromic acid is known only in soln., and combined in the form of bromates. The bromates are formed by adding an excess of bromine to alkali lye ; the alkali bromide and bromate are formed analogous to the corresponding reaction with chlorine. According to C. Löwig,[13] when bromine chloride is added to alkali lye so long as the colour disappears alkali chloride and bromate are formed. The lower solubility of the bromate enables it to be separated from the chloride and bromide. A. J. Balard prepared bromic acid by decomposing barium bromate with the right quantity of sulphuric acid, and decantiug the clear soln. from the precipitated barium sulphate. Any excess of sulphuric acid can be removed by baryta water. C. F. Rammelsberg failed to prepare the acid free from either baryta or sulphuric acid. J. S. Stas oxidized potassium bromide by passing chlorine into an alkaline soln. of the salt : $KBr+6KOH+3Cl_2=KBrO_3+6KCl+3H_2O$. C. Löwig passed chlorine into a soln. of potassium carbonate until it began to give off bubbles of gas, and then introduced bromine ; he also fused potassium bromide with the chlorate, and separated the bromate and chloride by fractional crystallization. A. Potilitzin found that by shakiug aq. soln. of sodium chlorate with bromine, there is no appreciable action after some hours, but in darkness, after 45 hours the formation of bromide, chlorate, and bromate can be detected. Bromine water transforms gold oxide into the bromate and bromide. H. Kämmerer heated iodic acid and potassium bromide and an excess of conc. aqua ammonia, at 110°, and found silver iodide and ammonium bromate were produced.

The acid is formed in many reactions with hypobromous acid ; for example, when

hypobromous acid is heated it is decomposed into a mixture of bromic and hydrobromic acids, and the latter can be removed by adding silver nitrate, and decanting the clear soln. from the silver bromide. A. Riche prepared it by the electrolysis of bromine water, or hydrobromic acid; the hydrobromic acid is oxidized by the nascent oxygen formed at the anode. As in the electrolytic production of chlorates, bromates are formed by the electrolysis of conc. soln. of alkali bromide between 40° and 50°. A little alkali dichromate is added (i) to produce a slight acidity in the soln. so as to accelerate the reaction: $2HBrO+NaBrO=NaBrO_3+2HBr$; and (ii) to prevent the reduction of bromate to hypobromite. Smooth platinum anodes and graphite cathodes are used. J. Sarghel obtained a better yield of bromate by electrolyzing soln. of calcium bromide than with soln. of alkali bromide.

H. Kämmerer made bromic acid by the action of bromine on silver bromate suspended in hot water: $5AgBrO_3+3Br_2+3H_2O=5AgBr+6HBrO_3$. The excess of bromine is driven off by heat, and the bromine acid soln. is decanted from the silver bromide. Bromine water converts hypochlorous acid into bromic acid and free chlorine. H. Kämmerer found that bromine converts a warm soln. of chloric acid into bromic acid, but a great deal is decomposed in the process. Bromine under bromine water is oxidized to bromic acid by leading in a current of chlorine monoxide: $5Cl_2O+Br_2+H_2O=2HBrO_3+5Cl_2$, and the dissolved chlorine can be driven off by heat. P. Lebeau also found that bromine water is oxidized by fluorine first to hypobromous and then to bromic acid.

The preparation of iodic acid and the iodates.—Iodic acid is obtained, either as free acid or combined in the iodates, by the action of oxidizing agents on iodine or iodine compounds, or by the decomposition of some of the other oxy-iodine compounds. J. L. Gay Lussac[14] showed that an excess of chlorine in the presence of much water converts finely divided iodine into iodic acid: $I_2+5Cl_2+6H_2O=10HCl+2HIO_3$, when the hydrochloric acid can be removed by the addition of silver oxide; if insufficient water be present some iodine chloride is formed; according to G. Sodini, at least twenty times as much water as iodine must be present. If a little alkali hydroxide be present, alkali chloride and iodate are formed, but if the alkali hydroxide be in excess some periodate is formed. G. S. Sérullas also showed that when iodine trichloride, moistened with alcohol or ether, is treated with water, iodic acid is formed: $2ICl_3+3H_2O=HIO_3+5HCl+ICl$. Alcohol removes the iodine monochloride and hydrochloric acid. J. von Liebig says that from 14 to 15 per cent. of the iodine is oxidized to iodic acid. J. von Liebig saturated water, holding finely divided iodine in suspension, with chlorine, neutralized the liquid with sodium carbonate, added barium chloride, and washed the precipitated barium iodate with water. H. Kämmerer treated a soln. of iodine in baryta water with chlorine—R. de Grosourdy used a soln. of barium chloride instead of baryta water.

Instead of chlorine as oxidizing agent, some of the chlorine oxides can be employed: H. Davy[15] used chlorine dioxide, and H. Kämmerer, chloric acid for the oxidation of iodine or iodine chloride. W. Flight oxidized iodine in alcoholic soln. by a hypochlorite soln.; and E. Reichhardt used bleaching powder. N. A. E. Millon, V. A. Jacquelin, and others employed the chlorates, for example, when iodine is heated with an aq. soln. of potassium chlorate, chlorine and potassium iodate and chloride are produced; H. Bassett represents the reaction by the equation: $5KClO_3+3I_2+3H_2O=3KH(IO_3)_2+2KCl+3HCl$; and on further evaporation both chlorine and iodine chloride may be formed: $KH(IO_3)_2+KCl+12HCl=2KCl+6H_2O+ICl+ICl.HCl+4Cl_2$. The presence of a small quantity of acid is necessary for the reaction. T. E. Thorpe and G. H. Perry consider that the main reaction is best represented: $2KClO_3+I_2=2KIO_3+Cl_2$. M. Schlötter found that when the concentration of the nitric acid is small, the reaction is represented: $5KClO_3+3I_2+3H_2O=5KIO_3+HIO_3+5HCl$; and when more acid is present: $2KClO_3+I_2=2KIO_3+Cl_2$. When the proportion of iodine to chlorate exceeds 1 : 2, the reaction is represented: $2KClO_3+I_2=2KIO_3+Cl_2$; and when the proportion is about 1 : 1, the reaction is: $KClO_3+I_2=KIO_3+ICl$. The nitric acid plays the *rôle* of

a catalytic agent: $I_2+6HNO_3+H_2O=2HIO_3+6HNO_2$; and $2HClO_3+6HNO_2=2HCl+6HNO_3$. According to J. S. Stas, if a mixture of potassium iodide and chlorate is heated to the temp. of decomposition, potassium iodide and chlorate are formed.

A. B. Lamb, W. C. Bray, and W. J. Geldard prepared iodic acid by directly oxidizing iodine by means of an acidified soln. of barium chlorate at 85°; and transformed the resulting barium iodate into iodic acid by means of sulphuric acid. The reaction between barium iodate is slow, possibly owing, as M. Guichard suggested, to the solubility of barium sulphate in the iodic acid. If an excess of sulphuric acid be employed, the iodic acid will be contaminated. G. P. Baxter found eleven crystallizations necessary to eliminate sulphate. If the iodic acid be contaminated with sulphuric acid, its subsequent dehydration for iodine pentoxide is attended by decomposition. The yields were 85–90 per cent. A. B. Lamb and co-workers believe that the best procedure is to reverse the preceding process. Barium chlorate is treated with sulphuric acid, and the iodine oxidized by the liberated chloric acid. A 10 per cent. soln. of chloric acid does not react with iodine at room temp., and after heating, even to boiling, the reaction is but slow; with 33 to 40 per cent. acid, the reaction starts immediately at room temp., and proceeds with explosive violence unless the mixture be cooled with an ice-bath. With 20–26 per cent. chloric acid, the reaction does not begin at once, but when once started (10–15 min., or by gentle heating), the iodine disappears in 15–20 min., and cooling is not necessary, nor are iodine fumes evolved during the reaction. A 3 per cent. excess of chloric acid maintains the iodine as iodic acid during evaporation, and removes any hydrogen chloride formed during the process as chlorine. The yield of powdered iodic anhydride was found to be 99·6 per cent. of the iodine used, and the process is simple, rapid, and economical.

H. Kämmerer also noticed that iodine transforms bromic acid into iodic acid and bromine: $2HBrO_3+I_2=2HIO_3+Br_2$. Similar remarks apply to the iodate of the alkalies and alkaline earths, for by heating an intimate mixture of the iodide and chlorate up to the temp. at which the chlorate gives off oxygen, the iodide is oxidized to iodate: $BaI_2+2KClO_3=Ba(IO_3)_2+2KCl$. According to J. L. Lassaigne, an aq. soln. of silver nitrate transforms iodine into iodic and nitric acids, and transforms iodine into iodic and nitric acids, and silver iodide; C. Weltzien treated dry silver nitrate with an alcoholic soln. of iodine; and H. Kämmerer treated silver iodate in the presence of water with iodine: $5AgIO_3+3I_2+3H_2O=6HIO_3+5AgI$. The aq. soln. of iodic acid is decanted and conc. by evaporation. Potassium iodate and free iodine are formed by treating moist potassium iodide with ozone; or by the action of ordinary oxygen at 400°–450°. According to M. Berthelot: $2KI+3O_2=2KIO_3+88·2$ Cals. W. Hempel, W. Linder, and W. Reinge oxidized iodides to iodates by potassium permanganate; I. Walz oxidized iodine to iodic acid by a mixture of chromic and sulphuric acids; chromic acid alone gives chromium iodate; J. J. Colin used gold oxide: $3I_2+5Au_2O_3+3H_2O=6HIO_3+10Au$; V. Auger used hydrogen peroxide for oxidizing iodine dissolved in hydriodic acid, in the presence of an excess of hydrochloric or hydrobromic acid: $2HCl+H_2O_2+2H_2O+Cl_2$; $I_2+3Cl_2=2ICl_3$; $5ICl_3+9H_2O\rightleftharpoons3HIO_3+15HCl+I_2$; and H. Marshall used persulphates for the same purpose.

In his great work on iodine, J. L. Gay Lussac[16] showed that the hydroxides of the alkalies, alkaline earths, magnesium, and zinc also react with iodine in aq. soln.: $6KOH+3I_2=5KI+KIO_3+3H_2O$, where only five-sixths of the converted iodine is in the form of iodate. The sparingly soluble potassium iodate can be separated from the iodide by fractional crystallization, or the mixed soln. of the two salts can be evaporated to dryness, and extracted with alcohol in which the iodide is fairly soluble, the iodate sparingly soluble. The residual iodate is dissolved in water, the soln. neutralized with acetic acid, and evaporated to dryness. The residue is then washed with alcohol to remove the potassium acetate. A similar transformation is effected by mercuric oxide suspended in water (J. J. Colin), or in

alcohol, benzene, acetone, or carbon tetrachloride (E. Lippmann), and silver oxide suspended in alcohol (G. S. Sérullas). Hypoiodous acid in alkaline soln. gradually passes into iodic acid : $KOI+2HOI=KIO_3+2HI$. The greater the excess of alkali present, the slower the reaction ; the higher the temp., and the free potassium iodide which is present, the faster the reaction. With an excess of potassium hydroxide the soln. is colourless, and the speed of the conversion[17] into iodate is approximately proportional to the product of the concentrations of the alkali hypoiodite, alkali iodide, and hypoiodous acid present ; if the iodine be in excess, the velocity increases with an increase in the concentration of the potassium hydroxide and of the iodine, and decreases with an increase in the concentration of the potassium iodide. The effect in the last two cases is the opposite of that produced when the potassium hydroxide is in excess, so that by gradually increasing the amount of potassium hydroxide the brown soln. becomes colourless, the velocity of formation of the iodate attains a maximum value, as illustrated in Fig. 10, where the numbers represent relative concentrations.

Conc. or rather fuming nitric acid is one of the most convenient oxidizing agents,[18] and iodic acid of a high degree of purity can be made by the oxidation of iodine by means of fuming nitric acid. Purified reagents are of course employed. The reaction proceeds at ordinary temp. with the formation of oxides of nitrogen and iodine nitrate. Heat hastens the reaction, and breaks up the iodine nitrate into nitric oxide, iodine and iodic acid. If a large excess of iodine be converted into iodic acid without loss, the iodic acid remains insoluble in the residual nitric acid. If the iodine be in large enough excess, the reaction proceeds until the nitric acid is so dil. by the production of water in the reaction, that it has no further action on the iodine even though the acid is conc. enough to keep the iodic acid sparingly soluble and to hold considerable quantities of iodine in soln. The yield of iodic acid by the action of nitric acid on iodine is not very great—about 4 per cent. ; a much greater yield—about 40 per cent.—is obtained by the action of nitric anhydride derived from a mixture of fuming nitric acid and phosphoric oxide. The process, though suitable for the occasional preparation of iodic acid on a small scale, is wasteful and expensive in large-scale operations.

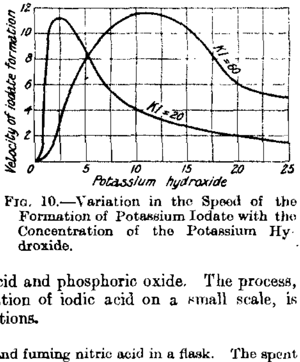

Fig. 10.—Variation in the Speed of the Formation of Potassium Iodate with the Concentration of the Potassium Hydroxide.

Iodic acid is best made by digesting iodine and fuming nitric acid in a flask. The spent acid is replaced by fresh acid from time to time until all the iodine is oxidized. Dissolved iodine can be recovered from the spent acid by dilution. The iodic acid so formed is drained and dissolved in the smallest possible quantity of dil. nitric acid, and the soln. evaporated in a dish of fused quartz so as to expel nitric acid and unchanged iodine. The residue is re-dissolved in water and again evaporated until a film of solid appears on the surface. This solid is not iodic acid, but probably a compound with less water. The soln. crystallizes slowly, and occupies some days. The solubility of the acid is high—75 per cent. at 25°—and the temp. coeff. of the solubility between 100° and 0° is small. Hence it is necessary to work up the mother liquors for successive crops of crystals. The crystals can be drained in a centrifugal machine. The iodic acid has frequently an aromatic odour which can be removed by a sufficient number of crystallizations.

A. Scott and W. Arbuckle obtained a 74 per cent. yield by using a round-bottomed flask with a long neck and a small flame so as to minimize the loss of iodine due to its vaporization with steam and the oxides of nitrogen. It required 10 days of 8 hrs. each to oxidize 100 grms., removing and renewing the spent acid each morning. By using iodine in fine powder with 10 to 12 times its weight of nitric acid of sp. gr. 1·5,

and leading a stream of oxygen through the liquid, 20 to 30 minutes' boiling suffices to convert all the iodine into iodic acid.

G. S. Sérullas obtained iodic acid, pure enough to leave no residue on ignition, by heating an aq. soln. of sodium iodate with an excess of sulphuric acid up to its b.p. Iodic acid separates from the filtrate, and the mother liquor, containing sodium sulphate, sulphuric acid, and a little iodic acid, can be poured away. The solid is washed with a little water. J. L. Gay Lussac made the acid by decomposing barium iodate with dil. sulphuric acid, and, after decanting the clear liquid from the precipitated barium sulphate, evaporating slowly until the liquid reached the point of crystallization. According to J. S. Stas, the crystals so obtained are always contaminated with sulphuric acid or baryta. The acid can be removed by boiling a soln. of the acid with a little barium iodide, filtering off the precipitated sulphate, and crystallizing out the iodic acid as before.

M. Guichard purified iodic acid by adding an equal volume of nitric acid (sp. gr. 1·33) to an aq. soln. of the impure acid, and concentrating the soln. until the iodic acid crystallized out. The operations are repeated until the acid is of the desired degree of purity. When the acid is crystallized in the presence of free sulphuric acid, some iodine pentoxide is usually present. G. S. Sérullas decomposed sodium iodate with an excess of hydrofluosilicic acid and evaporated the filtrate to dryness. In the latter case the iodic acid leaves a non-volatile residue when ignited. Hypoiodous acid, and aq. soln. of iodine tetroxide, and of periodic acid decompose with the formation of iodic acid. Similar remarks apply to the corresponding salts. A. Riche[10] prepared a soln. of iodic acid by the electrolysis of hydriodic acid, or water in which iodine was suspended. Iodine is oxidized by the oxygen developed on the anode. As with the chlorates and bromates, alkali iodates can be formed by the electrolysis of soln. of alkali iodides, and there is a very rapid conversion of iodides to iodates even in alkali soln. The conditions which favour the formation of iodate are increasing temp., and concentration of the iodide, and decreasing alkalinity of the soln.

A. Hantzsch also made iodic acid by the hydrolysis of azoimide iodide, N_3I, where the intermediate product is hypoiodous acid: $H_2O+N_3I=HOI+N_3H$; followed by: $5HOI=2H_2O+2I_2+HIO_3$.

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§ 12. The Properties of Chloric, Bromic, and Iodic Acids and their Salts

Chloric and bromic acids are not known in a free state, but only in aq. soln. and in the form of their salts. Iodic acid occurs as a white powder and in colourless crystals. Chloric and bromic acids form colourless aq. soln. which, by evaporation in vacuo, can be conc. to syrupy viscid liquids which first redden and then bleach blue litmus. When cold the aq. soln. have no smell, but when warm, chloric acid has a smell recalling that of nitric acid. The taste is like that of a strong acid. The conc. soln. of chloric acid does not crystallize when cooled to $-20°$. The soln. are stable when dil., and become less stable as the concentration increases. Soln. of bromic acid can be conc. on a water-bath until they contain between 13 and 14 per cent. of $HBrO_3$; when the attempt is made to concentrate further, the soln. begins to decompose, giving off oxygen and bromine. When the concentration is conducted under reduced press., in the cold, the decomposition does not begin until

the liquid contains about 50·6 per cent. of $HBrO_3$. The molecular formula of such a soln. corresponds with the *heptahydrated bromic* acid, $HBrO_3+7H_2O$, and accordingly H. Kämmerer thought that this corresponded with a definite hydrate, *although the evidence is not worth very much. Similar remarks apply to soln. of* chloric acid. When the soln. has a density of 1·282 at 14·2°, its composition corresponds with $HClO_3+7H_2O$. If the attempt be made to concentrate the solution further, by evaporation in the cold, *in vacuo* over sulphuric acid, the acid decomposes tumultuously: $8HClO_3=4HClO_4+2H_2O+3O_2+2Cl_2$, until its concentration approximates to $HClO_3+4\frac{1}{2}H_2O$. When the attempt is made to distil aq. soln. of chloric acid, almost pure water first passes over, then chlorine and oxygen gases are evolved, and perchloric acid remains behind.[1] According to W. S. Hendrixson, a 2·5*N*-soln. of chloric acid can be heated to 95° without decomposition ; the reports that chloric acid decomposes above 40° appear to be based on the use of impure acid—probably *containing hydrochloric acid which would decompose the chloric acid—or of a highly* conc. acid. Bromic acid soln. are also stated to decompose about 40°. Iodic acid decomposes at 110° into an anhydro-acid, as illustrated in Fig. 11. Aq. soln. of iodic acid resemble those of chloric and bromic acids, but when the conc. syrupy liquid was cooled, N. A. E. Millon obtained a crystalline powder ; and by slow evaporation below 60°, J. C. G. de Marignac and C. F. Rammelsberg obtained well-developed prismatic crystals terminated by pyramidal faces, and belonging to the rhombic system, with the axial ratios $a:b:c=0·9388:1:1·3181$, according to J. Schabus.[2] J. C. G. de Marignac showed that these crystals have a composition corresponding with HIO_3, and not, as J. Schabus thought, I_2O_5. J. C. G. de Marignac says that he succeeded *la seule fois* in obtaining crystals in the form of hexagonal plates belonging to the rhombic system with the axial ratios: $a:b:c=0·6399:1:1·1994$, and angular measurements approaching the values recorded by C. F. Rammelsberg. This makes it appear as if iodic acid may be dimorphous, but as C. F. Rammelsberg stated, the dimorphism has not yet been established. The optical properties of J. Schabus' crystals have been studied by J. Gruhlich and V. von Lang. E. Groschuff prepared a hygroscopic amorphous mass of iodic acid as an under-cooling soln. The crystalline forms are not deliquescent. According to H. Croft, when syrupy iodic acid is evaporated over sulphuric acid it forms ozone at the moment of crystallization.

According to H. Kämmerer,[3] the **specific gravity** of a 19·00 per cent. soln. of chloric acid is 1·128 ; of a 23·82 per cent. soln., 1·161 ; and of a 39·98 per cent. soln., 1·262—all at 14° ; and, according to R. Reyher, at 25° (water at 25° unity) the sp. gr. of soln. with *N*-mol. per litre is *N*-soln., 1·0485 ; $\frac{1}{2}N$, 1·0244 ; $\frac{1}{4}N$, 1·0126 ; and $\frac{1}{8}N$, 1·0064. E. Ruppin found a kilogram of the $\frac{1}{2}N$-soln. of chloric acid had a sp. gr. 1·0223 at 25°.

According to A. Ditte,[4] the sp. gr. of solid iodic acid is 4·629 at 0°, and 4·816 at 50·8° ; the sp. gr. of a sat. aq. soln. at 12·5° is 2·842 ; H. Kämmerer gives 2·1629 at 13°, and E. Groschuff gives 2·4256 at 13·5° (water at 4° unity) and 2·4711 at 18°. J. Thomsen makes the sp. gr. of aq. soln. containing *n*-mol. of water per mol. of iodic acid—HIO_3+nH_2O—to be

n	10	20	40	80	160	320
Sp. gr.	1·6609	1·3660	1·1945	1·1004	1·0512	1·0258
	34·3	31·4	30·1	29·5	27·2	26·8

where the last line refers to the increase in the mol. vol. of the dissolved acid per mol. of water ; hence a contraction occurs when soln. of iodic acid and water are mixed. J. Thomsen represents the mol. vol. v of aq. soln. HIO_3+nH_2O at 17° by the formula $v=18n+39·1-13·1n/(18+n)$. H. Kämmerer gives the following data for the sp. gr. of soln. of iodic acid at 14° :

I_2O_5 per cent.	1	10	20	30	40	50	60	65
Sp. gr.	1·0053	1·0525	1·2093	1·3484	1·5371	1·7356	1·9954	2·1269

R. Rea's values for the specific **viscosity** of normal soln. of chloric acid at 25° is 1·0520; for ½N-soln. 1·0255; for ¼N-soln. 1·0145; and for ⅛N-soln. 1·0059.

According to A. Ditte,[5] the **coefficient of thermal expansion** of solid iodic acid from 0° to 50·8° is 0·0002242; and the **specific heat,** 0·1625. A. Ditte also states that soln. of iodic acid sat. at 12·5°, boils at 104°; and H. Kämmerer that the soln. sat. at 13°, boils at 100°, and freezes at −17°. According to E. Groschuff, sat. soln., with $I_2O_5.HIO_3$ as solid phase, boils between 111° and 112° at from 766 mm. to 775 mm. press. According to H. Lescœur, the vap. press. of a soln. of iodic acid sat. at 20° is 11·6 mm. The mol. wt. determinations of A. Rosenheim and O. Liebknecht from the raising of the **boiling point** of soln. of iodic acid give a mol. wt. of 143 for soln. with 3·31 grms. of HIO_3 in 100 grms. of water and 202 for soln. with 29·95 grms. of HIO_3. J. H. van't Hoff's factor in the former case is i=1·23; and in the latter 0·87. This indicates that at the b.p. dil. soln. contain partially ionized monobasic HIO_3, and more conc. soln. the polymerized acid, possibly $H_2I_2O_6$. E. Groschuff also determined the factor i by the **freezing-point** method. With soln. containing 0·5911 grm. of HIO_3 per 100 grms. of water, the mol. wt. was 101·3 and i=1·737; with soln. containing 13·58 grms. of HIO_3, the mol. wt. was 170, and i=1·035; and with soln. containing 245·3 grms. of HIO_3, the mol. wt. was 370·5, and i=0·475, again showing that in conc. soln. the iodic acid is probably polymerized to $H_2I_2O_6$ and $H_3I_3O_9$—the dihydro-iodate, $KH_2I_3O_9$, can be regarded as a salt of the polymerized acid, $(HIO_3)_3$. In dil. one per cent. soln. the molecule of the acid seems to be normal HIO_3. Anhydro-iodic acid can be regarded as a derivative of the polymerized acid: $H_3I_3O_9=H_2O+I_2O_5.HIO_3$; and a further stage in the decomposition at 190°–200° is represented $2H_3I_3O_9=3H_2O+3I_2O_5$.

N. A. E. Millon (1843)[6] showed that the dehydration of iodic acid, HIO_3, occurs in two stages. By keeping the acid for a long time between 30° and 40° in dry air, or by heating it rapidly at 130°, it loses two-thirds of its water; and the remaining third at 170°. The intermediate product, said N. A. E. Millon, is a definite hydrate of the composition $I_2O_5.\frac{1}{3}H_2O$. This corresponds with the **anhydro-iodic acid,** $I_2O_5.HIO_3$. C. F. Rammelsberg (1844) believed that on dehydration, the acid passes directly into the anhydride; and A. Ditte (1870) and H. Lescœur (1890) found the vap. press. of Millon's intermediate product is the same as that of a mixture of iodic acid and the anhydride, a fact which made it appear as if the intermediate product is nothing more than effloresced iodic acid. E. Groschuff (1905), and G. P. Baxter and G. S. Tilley (1909), have confirmed the observation of N. A. E. Millon that the first product of the dehydration of iodic acid is an anhydro-acid with the composition $I_2O_5.HIO_3$. If iodic acid be rapidly heated, it melts at 110° with the separation of a solid phase, $I_2O_4.HIO_3$; if the acid be slowly heated to 110°, it dehydrates completely without fusion, forming pentoxide, I_2O_5, if the time of heating be sufficiently prolonged. The heating curve shows a terrace between 110° and 190°, corresponding with the existence of the intermediate phase, $I_2O_5.HIO_3$; and G. P. Baxter and G. S. Tilley mentioned one case of superheating without the appearance of this phase. H. Kämmerer reported the formation of hexagonal crystals of a *4½-hydrated iodic acid*, $HIO_3.4\frac{1}{2}H_2O$, by cooling sat. soln. to −17°; these crystals fuse at −15°. E. Groschuff could find no evidence of the existence of Kämmerer's hydrate, or of any hydrate other than Millon's $I_2O_5.HIO_3$. Millon's acid passes into ordinary iodic acid in the presence of water. It is insoluble in alcohol; and boiling alcohol dissolves only a trace. According to M. Berthelot,[7] the heat of soln. of one part of the acid in 45 parts of water at 12° is −4290 cals. In addition to anhydro-iodic acid prepared by N. A. E. Millon, $I_2O_5.HIO_3$, a second anhydro-iodic acid has been reported by P. Chrétien[8] as resulting from the soln. of an excess of iodic acid in a syrupy soln. of phosphoric acid at 150°, and slowly cooling the soln.; or by the cooling of a soln. of iodic acid in sulphuric acid containing between 4 to 5 mols. of H_2O per mol. of H_2SO_4. The acid separates in crystalline plates. The analysis corresponds with $2I_2O_5.H_2O$, that is, $I_2O_5.2HIO_3$, or $H_2I_4O_{11}$. According to M. Berthelot, its heat of soln. is $2I_2O_5.H_2O+1700H_2O=-5720$ cals. at 12°.

The individuality of this acid has not yet been established. According to H. Lescœur (1889), the crystals of iodic acid deposited from its soln. in dil. nitric acid are *monohydrated iodic acid*, $HIO_3.H_2O$; from soln. in conc. nitric acid, anhydrous iodic acid, HIO_3; and from soln. of nitric acid of intermediate conc., mixtures of monohydrated and anhydrous iodic acid.

The **heat of formation** of chloric acid deduced by J. Thomsen from the reduction of chloric acid with sulphur dioxide, is $H+Cl+3O+aq.=HClO_3aq.+23·9$ Cals., and 24·0 Cals. from the heat of decomposition, $KClO_3=KCl+3O+9·7$ Cals. M. Berthelot found 20·5 Cals. from the reduction of barium chlorate with sulphur dioxide. From the second of J. Thomsen's values: $2Cl+5O+aq.=2HClO_3+10·2$ Cals. For bromic acid, Br_2 (liquid)$+5O+aq.=2HBrO_3aq.-49·6$ Cals. (M. Berthelot); and $-43·52$ Cals.; Br_2 (gas)$+5O+aq.=2HBrO_3aq.-42·2$ Cals. (J. Thomsen).[9] $H+Br+3O+aq.=HIO_3+12·42$ Cals. For iodic acid, $I_2+5O+Aq.=2HIO_{3aq.}+43·237$ Cals.; $H+I+Aq.=HIO_3+55·797$ Cals.; $I_{solid}+3O+H=HIO_3+59·8$ Cals.; $I_2O_5+Aq.=2HIO_3aq.+2·54$ Cals. The heats of formation of aq. soln. of the three acids HX decrease as the at. wt. of the halogen X increases —$HCl_{aq.}$, 39·32 Cals.; $HBr_{aq.}$, 28·38 Cals.; $HI_{aq.}$, 13·17 Cals.; but with the HXO_3 acids, the heats of formation decrease from chlorine to bromine, and then increase very markedly in passing from bromine to iodine—$HClO_{3aq.}$, 23·94 Cals.; $HBrO_{3aq.}$, 12·42 Cals.; and $HIO_{3aq.}$, 55·8 Cals. Similar results are obtained with the corresponding salts. Thus, with the potassium salts, KCl, 105·61 Cals.; KBr, 95·31 Cals.; and KI, 80·13 Cals.; and also with $KClO_3$, 95·84 Cals.; $KBrO_3$, 84·062 Cals.; and KIO_3, 124·489 Cals. The **heats of neutralization** of chloric, bromic, and iodic acids in dil. soln. are nearly the same, and approximate 13·8 Cals., corresponding with the value typical of the stronger acids. A. R. Olson calculated the free energy of the reaction: $3Cl_2aq.+3H_2O=6H^{\cdot}+5Cl'+ClO'_3$ at 25° to be 6640 cals., and the heat of formation of the chlorate ion: $0·5Cl_2(gas)+1·5O_2+\ominus=-1374$ cals. at 25°.

Aq. soln. of chloric, bromic, and iodic acids are decomposed by the electric current with the separation of oxygen and the halogen at the anode.[10] Hypochlorous acid is formed in the case of chloric acid. W. Ostwald's values[11] for the **molecular conductivities** λ of aq. soln., chloric, bromic, and iodic acid in v litres of water at 25°, are:

v	2	8	32	128	512	1034	4096
$HClO_3$	77·9	82·3	85·3	87·9	88·7	88·6	85·7
$HBrO_3$	—	—	79·4	84·1	87·4	88·4	88·8
HIO_3	42·57	59·0	72·3	80·2	81·8	83·1	81·8

The maximum value for chloric acid is 88·7; accordingly, also, 88 per cent. of the acid in $\frac{1}{2}N$-soln. is ionized. The conductivities of chloric, perchloric, and nitric acids are of the same order of magnitude. Bromic acid thus has a lower conductivity, and is therefore a weaker acid than hydrobromic acid, but stronger than iodic acid; and iodic acid is weaker than hydriodic acid. The conductivities and the lowering of the f.p. of soln. of chloric, bromic, and iodic acids point to the respective formulæ $HClO_3$, $HBrO_3$, and HIO_3; but iodic acid is polymerized in conc. soln. The molecular conductivity of soln. of iodic acid $v=1$ rises from 102 at 0° to 223 at 75°; for $v=2$ from 126 at 0°, to 275 at 75°, and 279 at 80°; and for $v=1024$, from 239 at 0° to 634 at 80°. J. H. van't Hoff's factor $i=1+(n-1)\lambda_v/\lambda_\infty$, where n is the number of ions, agrees with the assumption that in dil. soln. the molecules are not polymerized, and in conc. soln., that they are polymerized to $H_2I_2O_6$. W. Ostwald also found the inversion constant of chloric acid for cane sugar ranges from 97·2 to 103·5 when the value for hydrochloric acid is 100. The velocity of the ClO_3'-ions is 587×10^{-8} at 25°, and 322×10^{-8} at 0°. F. Kohlrausch's values for the mobilities of the ClO_3', BrO_3', and IO_3'-ions are respectively 55, 46, and 33·9. G. N. Lewis and M. Randall give for the free energy of the reaction: $I_{solid}+3H_2O_{liquid}=6H^{\cdot}+IO_3'$, 137·59 Cals. at 25°; for $I_{solid}+\frac{3}{2}O_2=IO_3'$, $-32·27$ Cals. at 25°; and for the BrO_3'-ion, 1·69 Cals.

E. Groschuff's **solubility** curves [12] of iodic acid in water per 100 grms. of soln. are indicated in Fig. 11.

	−14°	0°	16°	80°	101°	110°	125°	160°
Grms. I_2O_5	69·1	70·3	71·7	78·3	80·8	82·1	82·7	85·9
Solid phase		HIO_3					$I_2O_5.HIO_3$	

The solubility of iodic acid in water, and the f.p. curve of soln. of this acid are indicated in E. Groschuff's equilibrium diagram, Fig. 11. The eutectic temp. is about −14° with 72·8 grms. HIO_3, or 69·1 grms. I_2O_5 per 100 grms. of soln.; or 8·29 mols. of H_2O per mol. of I_2O_5. The transition temp. of HIO_3 into the anhydro-iodic acid, $I_2O_5.HIO_3$, is 110° when the soln. has 86·5 grms. of HIO_3, or 82·1 grms. of I_2O_5 per 100 grms. of soln.; or 4·05 mol. of water per mol. of I_2O_5. The conversion of $I_2O_5.HIO_3$ into iodine pentoxide, I_2O_5, is between 190° and 200°—probably 196°—the exact temp. is difficult to determine on account of the slowness of the change. The solubility at −19° is 72·3. There is no sign of hydrates, $2HIO_3.9H_2O$, and of $HIO_3.5H_2O$, reported by H. Kämmerer.

Iodic acid is much less soluble in *nitric acid* than in water; the decrease is more marked at 0° than at 60°. For example, E. Groschuff gives

	0°	20°	40°	60
Water	74·1	75·8	77·7	80·0
27·73 per cent. HNO_3	18	21	27	38
40·88 per cent. HNO_3	9	10	14	18

Iodic acid readily forms under-cooled soln. with water and with nitric acid. The solubility becomes very small as the conc. of the nitric acid increases, a fact noted by G. S. Sérullas in 1830. The presence of *sulphuric acid* also diminishes the solubility of iodic acid, but there is a reaction between these two reagents—*vide infra.*

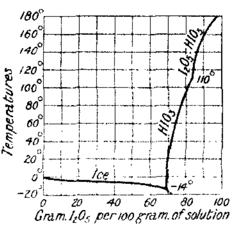

FIG. 11.—Equilibrium Diagram of the Binary System Iodine Pentoxide and Water.

N. A. E. Millon found iodic acid to be insoluble in absolute *alcohol*, but 87 per cent. alcohol dissolves almost half its weight of iodic acid; the acid is also insoluble in *acetic acid, ether, chloroform, carbon disulphide*, and in *hydrocarbons*.

The decomposition of chlorates, bromates, and iodates by heat.—*Vide* oxygen. The action of heat on chlorates either liberates the whole of the oxygen, and leaves a residue of the chloride—*e.g.* the chlorates of potassium, sodium, barium, mercury, and silver—or, if the metal has a greater affinity for oxygen than for chlorine, five-sixths of the oxygen and all the chlorine is liberated, and a metal oxide or a mixture of oxide and chloride remains—*e.g.* the chlorates of magnesium, zinc, and aluminium. According to M. Berthelot, $KClO_3 \rightarrow KCl + 3O - 11·0$ Cals. The case of potassium and sodium chlorates has been discussed in connection with the preparation of oxygen. A. Potilitzin [13] has studied the decomposition of barium and strontium chlorates; W. H. Sodeau, calcium, silver, and lead chlorates; and D. K. Dobroserdoff, aluminium chlorate. The case of the bromates is quite similar,[14] and J. S. Stas found that even with the alkali bromates, traces of bromine accompanied the oxygen. According to M. Berthelot, $KBrO_3 \rightarrow KBr + 3O - 11·1$ Cals. The decomposition of barium and strontium bromates has been studied by A. Potilitzin; and of aluminium bromate by D. K. Dobroserdoff. Barium bromate begins to decompose about 260°–265°, and the decomposition is vigorous about 300°. Iodates decompose in a general way similar to the chlorates and bromates, but at a rather higher temp. According to M. Berthelot, $KIO_3 \rightarrow KI + 3O - 44·1$ Cals. C. F. Rammelsberg [15] says that at no stage in the decomposition is any periodate formed, and that the solid residue of the action with potassium iodate and with barium iodate contains both

oxide or peroxide, and an iodide or an oxyiodide, but E. H. Cook showed that although a little iodine (0·308 per cent.) may be evolved during the decomposition of potassium iodate no periodate is formed, and the residue is potassium iodide. C. F. Rammelsberg's residues probably contained undecomposed iodate. According to C. F. Schönbein, if the iodate is mixed with pyrolusite or graphite, the products of the reaction are iodine, oxygen, and potash.

According to J. L. Gay Lussac,[16] aq. soln. of chloric acid do not decompose in **light,** but according to N. A. E. Millon, when conc. chloric acid is kept for two *months* beside conc. sulphuric acid, some perchloric acid is formed. A. Pedler exposed $0{\cdot}2N$, $0{\cdot}1N$, $0{\cdot}05N$, and $0{\cdot}03N$-soln. of chloric acid for 15 days to tropical sunshine, and as a result found that the decomposition of the acid in dil. soln. is negligibly small, and this acid may be regarded as an end-product of the action of sunlight on chlorine water. M. Berthelot states that iodic acid is decomposed by exposure to sunlight—at ordinary or at elevated temp. Soln. of chlorates and bromates are fairly stable in light, but they are slowly decomposed by ultra-violet rays which are normally cut off by the glass of the containing vessel. The amount of salt decomposed in a given time is proportional to the time of exposure in the case of soln. from $0{\cdot}5N$- to $0{\cdot}02N$-strength. The presence of sugar accelerates the reaction, and this the more with bromates than chlorates.[17]

Chloric acid decomposes **organic substances** very rapidly often with inflammation—*e.g.* G. S. Sérullas soaked filter paper with chloric acid, and found that it spontaneously inflamed, and litmus paper was first reddened and then bleached; bromic and iodic acids behave similarly towards litmus. According to W. Feit and K. Kubierschky,[18] bromic acid is a stronger **oxidizing agent** than either chloric or iodic acid. It transforms **sulphur** into sulphuric acid faster than chloric, iodic, permanganic, chromic or nitric acid, bromine water, or hydrogen peroxide. Sulphur is not attacked by cold iodic acid, but in a sealed tube at 150° it forms sulphuric acid; **selenium** under similar conditions is oxidized at 200°; white and red **phosphorus** are immediately attacked, forming phosphoric acid with the liberation of iodine.[19] **Arsenic** forms arsenic acid. Many organic substances are quantitatively oxidized by bromic, chloric, and iodic acids to carbon dioxide and water—*e.g.* with oxalic acid: $5H_2C_2O_4+2HBrO_3=10CO_2+6H_2O+Br_2$. An excess of oxalic acid with iodic acid behaves similarly in the presence of sulphuric acid; and if the excess of oxalic acid or the liberated iodine be titrated the iodic acid can be quantitatively determined. Similar remarks apply to the chlorates, bromates, and iodates. When chlorates, bromates, or iodates are mixed with combustible or oxidizable substances—carbon, phosphorus, sulphur, base metals—copper, aluminium, arsenic—metal sulphides, sugar, etc.—the mixtures are very prone to decompose with explosive violence when struck with a hammer or heated.

Mixtures of chlorates with such materials must not be ground together with a pestle and mortar. The materials should be ground separately, and then carefully mixed on paper with a feather. Phosphorus in contact with a chlorate may explode spontaneously. Thus if a drop of soln. of phosphorus in carbon disulphide be allowed to fall on a little potassium chlorate, a loud explosion occurs as soon as the carbon disulphide has evaporated. The red phosphorus in the mixture on the side of a box of safety matches gives a series of sparks when a crystal of potassium chlorate is rubbed thereon, and serious accidents have occurred as a result of the accidental rubbing of tabloids of potassium chlorate against the sides of a match-box in the pocket.

The violence of the explosion is feebler with iodates than it is with chlorates or bromates. The chlorates transform **lead oxide** to the dioxide; **manganese oxide** in fused alkalies to manganates; etc. Ammonium iodate explodes when heated alone. Chloric, bromic, and iodic acids with their salts are energetic oxidizing agents.

The oxidizing action of potassium chlorate in neutral or sligbtly acid soln. is greatly facilitated by the presence of traces of osmium tetroxide, OsO_4.

Hydrogen sulphide is oxidized by adding chloric acid to water, sulphuric acid,

and hydrochloric acid; with bromic acid, the reaction is represented: $5H_2S+8HBrO_3=4H_2O+5H_2SO_4+4Br_2$—if the hydrogen sulphide be in excess, some free sulphur is formed. for, with iodic acid, not only is there the direct reaction: $5H_2S+8HIO_3=4H_2O+5H_2SO_4+4I_2$, but there is a reaction between the iodine and hydrogen sulphide: $H_2S+I_2=2HI+S$. According to J. W. Slater,[20] hydrogen sulphide does not act on aq. soln. of chlorates; but according to A. J. Balard, the bromates decompose the gas into water, bromine, sulphate, and sulphur; iodates, according to H. Rose, behave in an analogous manner. With **thiosulphuric acid,**[21] the halogen and sulphuric acid are formed; for example, with bromic acid: $5H_2S_2O_8+8HBrO_3+H_2O=10H_2SO_4+4Br_2$.

Sulphur dioxide is oxidized by chloric, bromic, and iodic acids, forming sulphuric acid and the free halogen: $2HBrO_3+5H_2SO_3=H_2O+5H_2SO_4+Br_2$. According to W. R. Hodgkinson and J. Young,[22] if sulphur dioxide be led over powdered potassium chlorate, chlorine dioxide is formed so long as the temp. does not rise over 60°; at a higher temp., there is a slight incandescence, and a white cloud of sulphur trioxide and chlorine is formed. Moist sulphur dioxide acts more rapidly than the dry gas; and if some organic substances are present, the action is more vigorous still. If a drop of a soln. of sulphur dioxide in ether or alcohol is dropped on a little powdered potassium chlorate, a white vapour rises, and then the mass explodes. According to J. L. Gay Lussac, aq. soln. of the bromates and iodates oxidize sulphur dioxide to a sulphate, free **sulphuric acid,** and the free halogens. The reaction between **sulphurous** and iodic acids or between **sulphites** and iodates: $2HIO_3+5SO_2+4H_2O=5H_2SO_4+I_2$, has attracted much attention,[23] because the iodine does not appear immediately the substances are mixed; there is a well-defined period of time—*period of induction*—between the moment the reacting substances are mixed and the moment iodine makes its appearance. H. Landolt showed that the duration of the interval is dependent upon the conc. of the soln.

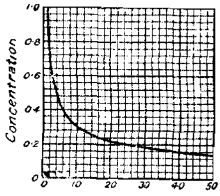

FIG. 12.—Relation between the Period of Induction and the Concentration of the Solutions.

H. Landolt's reaction can be demonstrated in the following manner: Dissolve 1·8 grm. of iodic acid in a litre of water; also prepare a litre of an aq. soln. of 0·9 grm. of sodium sulphite, $Na_2SO_3.7H_2O$; 10 per cent. sulphuric acid, and 9·5 grms. of starch made into a paste with hot water. Add 100 c.c. of each soln. to separate beakers; and mix the two. Note the time when the soln. are mixed. Count the seconds which pass before the starch blue appears. Dil. each soln. to 0·8, 0·6, 0·4, 0·2th of its former concentration, and repeat the experiments with the dil. soln. Plot the results as has been done in Fig. 12. If the concentration and temp. be constant, the same results can always be reproduced.

It is supposed that the first action may be due to the reduction of iodic to iodous acid, HIO_2, thus: $H_2SO_3+HIO_3=HIO_2+H_2SO_4$; then iodous to hypoiodous acid: $H_2SO_3+HIO_2=HOI+H_2SO_4$; and then to hydriodic acid: $H_2SO_3+HOI=HI+H_2SO_4$. This, however, is largely hypothesis. In any case the first stage of the reaction results in the reduction of the iodic acid to hydriodic acid: $3H_2SO_3+HIO_3=3H_2SO_4+HI$; when all the sulphurous acid has been oxidized, this reaction is followed by a reduction of the hydriodic acid by the excess of iodic acid: $HIO_3+5HI=3H_2O+3I_2$. If the sulphurous acid is in excess, there is the reverse, the liberated iodine reforms hydriodic acid: $H_2SO_3+H_2O+I_2=H_2SO_4+2HI$. The first reaction—oxidation of sulphurous acid—must be nearly completed before the second one—oxidation of hydriodic acid—can start, because, as indicated above, the iodine with sulphurous acid reforms hydriodic acid. Since the maximum amount of iodic and sulphurous acids are present at the start, the first-named reaction must be fastest at the beginning, and afterwards gradually slow down.

Again, since the velocity of a reaction is proportional to the amount of the reacting substances present in the system, the second reaction will be the slowest at the start, and gradually become faster. The speed of formation of the iodine is therefore the resultant velocity of two consecutive reactions; and the belated appearance of the iodine—the period of induction—corresponds with the time required for the first reaction to make enough hydriodic acid to enable the second reaction to make sufficient iodine to colour the starch.

The successive steps in the reduction of iodic acid to iodine can therefore be symbolized: $HIO_3 \rightarrow HI \rightarrow I_2$, where HI represents an *intermediate compound*—characteristic of consecutive reactions generally.

The time of the induction is dependent upon two independent constants, K_1 and K_2. If K_1 be the velocity constant of the first reaction, K_2 that of the second, J. Eggert has shown that the time of the induction t can be calculated with a satisfactory approximation to the observed values by the formula:

$$\text{Time of induction, } t=\frac{1}{K_2-K_1}\log_e\frac{K_2}{K_1}$$

L. Berczeller has shown that the presence of acids, chlorides, bromides, iodides, thiocyanates, and morphine accelerate the reaction; while the presence of tartrates, sulphates, oxalates, carbonates, mercuric chloride, bromide, iodide, and cyanide, most alkaloids, colloids, proteins, etc., inhibit the reaction. Hydrocyanic acid, unlike other acids, also inhibits the reaction. A. Skrabal has shown that Landolt's reaction has a temp. coeff. greater than unity, so that the velocity of the reaction increases with a rise of temp.; but if the system contains an excess of sodium sulphate, the temp. coeff. is less than unity, and the velocity of the reaction decreases with a rise of temp.

O. Liebreich[24] showed that the reaction is of special interest, because it exhibits a **dead space in reacting systems,** *i.e.* there is a place in this reacting system where little or no reaction takes place. When alkalies act upon chloral, a white precipitate of chloroform appears, but no formation of chloroform appears if the reaction takes place in fine capillary tubes; while if the reaction occurs in a test tube, a thin film of liquid quite clear and free from chloroform appears just at the upper surface. It is supposed that the reaction is modified at the boundary layers by the surface tension of the liquid. J. W. Gibbs proved that the surface layer of a liquid will in general differ in composition from the body of the liquid, and for dil. soln. he proved thermodynamically that *the surface layers of a solution are richer or poorer in solute according as the addition of the solute lowers or raises the surface tension.* J. J. Thomson has further shown that *if surface tension of a soln. increases as a chemical reaction progresses, capillarity will tend to stop the reaction; and conversely, if the surface tension diminishes as the reaction progresses, capillarity will tend to increase the reaction.* Otherwise expressed:

The effect of the forces between the molecules of a liquid will be to promote any change which diminishes the surface tension at a fresh surface. For example, if any chemical action will diminish the surface tension, that action will take place more readily at the fresh surface than in the body of the liquid. If the liquid be a salt soln. the salts will flock to the surface if the surface tension of a conc. soln. is less than that of a dil. one, and recede from it if it is greater. If two isomeric compounds have different surface tensions, then spraying or bubbling air through a mixture will increase the proportion of the one with the smaller surface tension. The molecules of a compound AB might split up at the surface layer into atoms, if a layer of dissociated atoms either mixed together or in separate layers would give a smaller surface tension than the undissociated liquid.

According to H. Kämmerer,[25] chloric acid reacts with **bromine,** giving only traces of bromic acid; but with **iodine** it forms iodic acid, and with **iodine chlorides** it furnishes iodic acid and chlorine; bromic acid is not affected by **chlorine**, but with iodine it forms iodic acid. When a soln. of potassium chlorate acidified with

nitric acid is treated with iodine, the main reaction is determined by the concentration of the nitric acid and of the iodine. With *dilute acid*, the main reaction is symbolized: $10KClO_3+6I_2+6H_2O=10KIO_3+2HIO_3+10HCl$; with *concentrated acid*: $2KClO_3+I_2=2KIO_3+Cl_2$ and $KClO_3+I_2=KIO_3+ICl$. By distilling iodine with potassium chlorate, F. Wöhler [26] obtained iodine chloride, and potassium chloride and iodate. A boiling soln. of potassium chlorate takes up the eq. of a gram-atom of iodine without discolouring the soln.; further additions of iodine colour the soln yellow and then brown, forming potassium iodate and iodine chloride. A. Potilitzin represents the reaction: $5KClO_3+3I_2+3H_2O=5KI+5HClO_3+HIO_3$, followed by $KI+HIO_3=HI+KIO_3$, and by $HI+HClO_3=HCl+HIO_3$. Sodium and barium chlorates behave similarly. Bromine acts on aq. soln. of the chlorates in darkness forming bromide, chlorine, and bromic acid. H. Kämmerer reported that chlorine exerts no action on bromates. According to A. Potilitzin, when chlorine is passed for 50 days through a sat. soln. of sodium bromate, in darkness, bromine is formed and the soln. contains the metal chloride, and chloric and bromic acids. The main reaction is represented: $5NaBrO_3+3Cl_2+3H_2O=5NaCl+5HBrO_3+HClO_3$. Chlorine and bromine do not act on iodic acid or the iodates. H. Schulze [27] found that most of the chlorides, bromides, and iodides when melted with potassium chlorate give the free halogen and metal oxide—the silver and mercury halides are not attacked. According to G. S. Sérullas, when a soln. of a mixture of potassium chlorate and iodic acid is evaporated, crystals of potassium iodate or of acid potassium iodate separate, and the mother liquid contains potassium chlorate and chloric acid.

J. L. Gay Lussac and L. N. Vauquelin noted that **hydrochloric acid** is decomposed by chloric acid into chlorine and water. An aq. soln. of potassium chlorate reacts slowly with dil. hydrochloric acid with the evolution of chlorine. The first stage of the reaction is probably: $HClO_3+2HCl\rightleftharpoons 3HOCl$, followed by a reaction between the hypochlorous and hydrochloric acids: $HCl+HOCl=H_2O+Cl_2$. The complete reaction is represented: $HClO_3+5HCl=3Cl_2+3H_2O$. Raising the temp. increases the rate of evolution of the gas; and the reaction is accelerated with platinum as catalytic agent. A conc. soln. of potassium chlorate, says R. Wagner, gives very little chlorine with dil. hydrochloric acid unless the mixture be warmed: $KClO_3+6HCl=KCl+3H_2O+3Cl_2$. L. von Pebal [28] and G. Schacherl have based a process for the preparation of chlorine on this reaction. Conc. hydrochloric acid with a chlorate furnishes chlorine dioxide, ClO_2, and chlorine: $2KClO_3+4HCl=2KCl+Cl_2+2ClO_2+2H_2O$. When a bromate is treated with hydrochloric acid, it forms bromine and chlorine: $2KBrO_3+12HCl=2KCl+Br_2+5Cl_2+6H_2O$. Conc. hydrochloric acid also decomposes the iodates to form water, chloride, free chlorine, and iodine chloride. The latter may form a double salt with the chloride: $KIO_3+6HCl=3H_2O+Cl_2+KCl.ICl_3$. R. Bunsen showed that in the reaction between potassium chlorate, potassium iodide, and conc. hydrochloric acid, three mols. of iodine are separated for every mol. of potassium chlorate decomposed. According to C. Winkler, an aq. soln. of potassium chlorate and iodide is very slowly decomposed with the separation of iodine by dil. hydrochloric acid; but if a considerable excess of the acid is used, the reaction may be completed at ordinary temp. by the decomposition of all the chlorate. Similar remarks apply if potassium bromide is used in place of the iodide. H. Ditz has founded a method for the quantitative determination of chlorates on this reaction. R. Luther has shown that a feebly acid soln. of potassium bromide and chlorate which develops bromine very slowly, completes the reaction very quickly if a vanadium salt be present.

A. J. Balard showed that bromic acid is decomposed by **hydrobromic acid** into bromine and water; by hydrochloric acid into water and bromine chloride; and by hydriodic acid into water and iodine bromide. There are nine reactions belonging to this set, namely, chloric, bromic, and iodic acids each with each of the three haloid acids—HCl, HBr, and HI. The kinetics of these reactions have been studied extensively.[29] W. Bray has shown that the velocity of the reaction between

potassium chlorate, potassium iodide, and hydrochloric acid is proportional to the concentration of the chlorate, and to the square of the concentration of the acid; and is a linear function of the concentration of the potassium iodide. The speed of the reaction is doubled every 8·6° rise of temp. The results are explained by assuming that the chloric acid is reduced by a slow reaction to chlorous and hypochlorous acid: $HClO_3+HCl=HOCl+HClO_2$, or $HClO_3+HI=HOI+HClO_2$; and the subsequent reduction of the hypochlorous (or hypoiodous) and chlorous acids proceeds very quickly. The reaction between potassium chlorate, iodide, and sulphuric acid has been investigated by J. McCrae.

The kinetics of the reaction between bromic acid and **hydriodic acid** have been investigated by W. Ostwald (1888), W. Meyerhoffer (1888), G. Magnanini (1890), etc.[30] W. Ostwald showed that the reaction between hydriodic and bromic acids is accelerated by the presence of various acids—arsenic, phosphoric, hypophosphorous, hyposulphurous, sulphuric, hydrochloric, nitric, chloric, perchloric, hydrobromic, lactic, formic, acetic, and propionic acids—at a rate which is roughly proportional to the affinity constants or the molecular conductivity of the added acid; hydrobromic acid accelerated the reaction at a faster rate than corresponded with the velocity constant. R. H. Clark has shown that the rate at which iodine is liberated in soln. containing potassium bromate, potassium iodide, and hydrochloric acid is proportional to the concentration, C_1, of the bromate, to the concentration, C_2, of the iodide, and to the square of the concentration, C_3, of the acid; otherwise expressed: Velocity of the reaction$=KC_1C_2C_3^2$, where K is the velocity constant; if potassium bromide is present in addition, the two halide salts are oxidized independently. The potassium tri-iodide formed by a secondary reaction slightly accelerates the reduction of the bromate. Raising the temp. 10° multiplies the rate of the reaction 1·85 times. W. Judson and J. W. Walker find the reaction between hydrobromic and bromic acid in the presence of an excess of sulphuric acid to be bimolecular. The simplest equation is $5HBr+HBrO_3=3H_2O+3Br_2$, apparently a seximolecular reaction. The difference is explained by assuming that the reaction takes place in different stages some of which are extremely rapid. For example, if the reaction occurs in three stages: (i) In the first stage, hypobromous and bromous acids are produced: $HBr+HBrO_3=HBrO+HBrO_2$; (ii) The hypobromous acid is reduced by the hydrobromic acid: $HBr+HBrO=H_2O+Br_2$; and (iii) The bromous acid is reduced by the hydrobromic acid: $HBrO_2+3HBr=2H_2O+2Br_2$. The reductions of the hypobromous and bromic acids are probably very fast reactions in the presence of a large excess of sulphuric acid, and the speed of the first reaction is alone accessible to measurement, and the change in the concentrations of the acid in view of the large excess present is negligible —hence C_3^2 is a constant; on the other hand, with the pure acids, the acidity of the soln. steadily decreases, and two weak acids—hypobromous and bromous—are formed, so that the reaction proceeds quadrimolecularly as found by R. H. Clark. R. Luther and G. V. Sammet tried to measure the equilibrium constant of the reaction: $HBrO_3+5HBr\rightleftharpoons3Br_2+3H_2O$, indirectly from the electromotive force of the cell $Pt[H^{\cdot}, BrO_3, Br_2]\|[Br_2, Br']Pt$, and found the extraordinarily small number $7·3\times10^{-34}$ at 25°. J. Sand found the equilibrium constant of the corresponding reaction with chloric acid: $HClO_3+5HCl\rightleftharpoons3Cl_2+3H_2O$, to be $6·0\times10^{-12}$; and with iodic acid: $HIO_3+5HI\rightleftharpoons3I_2+3H_2O$, $2·8\times10^{-47}$ at 25°, and $5·2\times10^{-42}$ at 60°. The reaction in acid soln. is virtually completed in favour of the compounds on the right side, and the left side in alkaline soln. Similar remarks apply to the reaction: $HBrO_3+5HI=3Br_2+3H_2O$.

According to H. Kämmerer,[31] chlorine and bromine have no action on iodic acid. E. Soubeiran found that iodic acid with hydrochloric acid produced water, iodine chloride, and chlorine; and J. L. Gay Lussac found that with hydriodic acid, it produced water and iodine; and with the iodides of the metals which form feeble basic oxides, iodic acid produces the metal oxide and iodine: $Zn(IO_3)_2+5ZnI_2=6ZnO+6I_2$. According to C. F. Roberts, iodine or potassium iodide and

iodic acid, in the presence of hydrochloric acid, form iodine chloride: $HIO_3 + 2KI + 5HCl = 3H_2O + 2KCl + 3ICl$; and: $HIO_3 + 2I_2 + 5HCl = 5ICl + 3H_2O$. The iodine chloride can be decomposed by alkali hydroxide: $6KOH + 5ICl = 5KCl + KIO_3 + 3H_2O + 2I_2$. O. Burchard[32] investigated the kinetics of the reaction between iodic and hydriodic acids, and found the speed to be greater than with bromic and hydriodic acids, and this in turn greater than with chloric and hydriodic acid. The reaction is accelerated by the hydrobromic, hydrochloric, nitric, and sulphuric acids, and to a much greater extent by hydriodic and iodic acids. S. Dushman[33] found the speed of the reaction between iodic and hydriodic acids to be proportional to the concentration of the iodic acid, to the second power of the acid, and to the 1·8 to 1·9th power of the hydriodic acid. The speed is increased 1·4 times per 10° rise of temp. If dil. hydrochloric or sulphuric acid is added to a mixed soln. of potassium iodide and iodate, the reaction: $KIO_3 + 5KI + 6HCl = 3I_2 + 6KCl + 3H_2O$, is completed, provided the amount of hydrochloric acid theoretically required is present; in fact, the quantity of iodine liberated is directly proportional to the amount of acid which is present. In consequence, H. Ditz and B. M. Margosches proposed to determine iodometrically the amount of free acid by this reaction, titrating the liberated iodine with standard sodium thiosulphate soln. The reaction is not complete with acetic, tartaric, and other organic acids, though it is with oxalic acid. The process is therefore not suited for organic acids. The reduction of the iodate, says S. Bugarsky, does not take place so readily if the potassium iodide be replaced by the bromide, nor again if the bromide be replaced by chloride. In the latter case, a considerable excess of free acid is needed for a complete reaction. Even carbon dioxide liberates some iodine when the gas is led into a mixed solution of iodide and iodate, but not into a mixed soln. of bromide or chloride and iodate.

According to A. Stock, if a mixture of **potassium iodide** and iodate be added to a slightly acid soln. of an aluminium salt, granular aluminium hydroxide and iodine are separated: $Al_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Al(OH)_3 + 3K_2SO_4 + 3I_2$. The reaction is complete only when the mixture is warmed on a water-bath, and the iodine separated by the addition of sodium thiosulphate. This reaction also works with iron and chromium, and has been used for the determination of aluminium, iron, and chromium; if the iron is in the ferrous condition it is simultaneously oxidized to the ferric state. The sulphates of tin, copper, nickel, cobalt, and zinc behave similarly. With zinc sulphate the reaction is represented: $15ZnSO_4 + 20KI + 4KIO_3 + 12H_2O = 3Zn_5(OH)_8SO_4 + 12K_2SO_4 + 12I_2$.

Sulphuric acid has no action on chloric or bromic acid provided the conc. acid does not heat the soln. to the temp. of its decomposition. Conc. sulphuric acid does not attack iodic acid below 15°; above 130°, N. A. E. Millon found that iodic acid is dehydrated by sulphuric acid and converted into iodine pentoxide. Sulphuric acid dissolves about one-fifth of its weight of iodic acid at 200°, and bubbles of oxygen are formed by the decomposition of the iodic acid, and crystals of the pentoxide are formed; at higher temp., the acid is decomposed. Dil. sulphuric acid with a soln. of a chlorate forms chloric acid. Similar results are obtained with dil. sulphuric acid and a bromate; and, according to J. L. Gay Lussac, with sulphuric acid and an iodate at about 100°. Conc. sulphuric acid with a chlorate gives chlorine dioxide, ClO_2, and perchloric acid, $HClO_4$—the former dissolves in the sulphuric acid colouring it orange yellow: $3KClO_3 + 3H_2SO_4 = 3KHSO_4 + HClO_4 + 2ClO_2 + H_2O$—the chlorine dioxide may cause an explosion, so that the experiment is to be performed with care on but a granule of the chlorate. When a bromate is treated with conc. sulphuric acid, bromine and oxygen, neither bromine dioxide nor perbromic acid, are formed: $KBrO_3 + H_2SO_4 = KHSO_4 + HBrO_3$; and $4HBrO_3 = 2Br_2 + 5O_2 + 2H_2O$. Conc. sulphuric acid gives no free iodine with the iodates if reducing agents be absent. If potassium iodide be also present, iodine is formed: $KIO_3 + 5KI + 3H_2SO_4 = 3I_2 + 3K_2SO_4 + 3H_2O$. Other reducing agents—*e.g.* hydrogen sulphide, sulphur dioxide, zinc, ferrous sulphate, etc.—in small quantities when

added to an acidified soln. of an iodate produce some iodide which then reacts as just indicated.

According to H. Ditz and B. M. Margosches, a conc. soln. of **boric acid** does not separate iodine from the mixture of iodide and iodate unless some glycerol, mannite, or dextrine be present; no iodine is obtained from a mixture of bromide and iodate even in the presence of glycerol. A. Hileman proposed to determine fluorine iodometrically from the reaction: $H_2SiF_6+5KI+KIO_3=6KF+3I_2+SiO_2+H_2O$.

Chloric, bromic, and iodic acids are not decomposed by **nitric acid.** Chloric and bromic acids oxidize **nitrous acid** to nitric acid; *e.g.* $5HNO_2+2HBrO_3=5HNO_3+H_2O+Br_2$; this reaction proceeds rapidly at ordinary temp., and is the base of a method for the quantitative determination of nitrites.[34] Aq. soln. of iodic acid oxidize nitric oxide, NO; nitrous acid, HNO_2; nitrogen peroxide, NO_2, forming iodine and nitric acid. The reaction occur only in the presence of much water. Nitric acid of greater sp. gr. than 1·45 is not reduced while dissolving iodic acid. Nitric acid of sp. gr. 1·4 dissolves potassium chlorate without coloration, and when the soln. is evaporated to dryness, chlorine and oxygen are evolved, and perchlorate is formed;[35] if the nitric acid contains some nitrous acid, the soln. is coloured yellow, and hydrochloric acid is formed. If a little sodium nitrite is added to a soln. of potassium chlorate acidified with nitric acid, the chlorate is reduced to chloride in about 10 minutes. Heated in sealed tubes with conc. nitric acid or fuming nitric acid potassium chlorate is quantitatively reduced. Bromates are decomposed by nitric acid with the evolution of oxygen, and the separation of bromine. When iodates are heated with nitric acid, the iodic acid is wholly or partially liberated from the base.

Phosphorous acid and **phosphine** are oxidized by chloric, bromic, and iodic acid to phosphoric acid. Iodic acid acts on phosphorus forming phosphoric acid, iodine, etc. A. Ditte[36] found that iodic acid converts powdered arsenic to arsenic acid, H_3AsO_4; and pieces of arsenic are attacked at about 30°, forming arsenic trioxide. Phosphoric acid partially dehydrates iodic acid without combination; but if iodic acid be added to a hot soln. of phosphoric acid boiling at 150°, the soln. deposits prismatic crystals of the complex **phosphatoiodic acid,** $P_2O_5.18I_2O_5.4H_2O$. The potassium, sodium, ammonium, and lithium salts of this acid have alone been prepared by P. Chrétien. According to R. Chenevix, chlorates are decomposed when heated with **phosphoric acid** or **arsenic acid,** but **arsenic trioxide** has no action on the chlorates. J. W. Slater also found that **phosphorus** reduces aq. soln. of potassium chlorate to the chloride, forming phosphoric and phosphorous acids; **arsenic** under similar conditions forms arsenate. **Phosphorus pentachloride,** PCl_5, has but little action on cold potassium chlorate, but when a mol. of phosphorus pentachloride is melted with three of potassium chlorate, chlorine and chlorine dioxide, and potassium chloride and phosphoryl chloride are formed.[37]

Chlorates, bromates, and iodates are reduced to the corresponding halide by zinc dust, aluminium, or Devarda's alloy—copper, 50; aluminium, 45; zinc, 5. In his study, *The action of chloric acid on metals*, W. S. Hendrixson[38] showed that the action may follow one or both of at least two courses: (i) The acid may dissolve the metal with the liberation of hydrogen in the same way as hydrochloric acid, and with very little oxidation: $2M+2HOCl=2MOCl+H_2$; and (ii) The acid may act as an oxidizing agent. The actual course of the reaction depends upon the nature of the metal and the concentration of the acid. He found no metal dissolves in the acid without the reduction of at least a portion of the acid. **Cadmium, copper, iron** disappear in the acid without the evolution of any gas whatever. D. Tommasi stated that **sodium amalgam** and **potassium amalgam** dissolve in cold chloric acid without the least reduction of the acid, but W. S. Hendrixson found that there is a slight reduction of the acid. **Mercury** alone, at 40°, is scarcely affected by the acid after four hours' treatment. When **magnesium** is dissolved, about one-twentieth of the amount dissolved reduces the acid, and the remainder forms magnesium chlorate with the evolution of an eq. amount of hydrogen.

According to J. L. Gay Lussac and J. J. Berzelius, chloric acid dissolves **zinc** with the evolution of an eq. amount of hydrogen; on the contrary, L. N. Vauquelin and M. J. Fordos and A. Gélis say that it dissolves with the reduction of the acid without the evolution of hydrogen; L. Gmelin says it dissolves both with the evolution of hydrogen and the reduction of the acid. D. Tommasi found that the acid is completely reduced by an excess of zinc and sulphuric acid, and zinc is used in the presence of sulphuric acid as reducing agent for converting chlorates to chlorides in analysis. W. S. Hendrixson found that with normal chloric acid about 33 per cent. of the dissolved zinc liberates hydrogen, and about 66 per cent. of the dissolved zinc reduces the chloric acid to chloride; with $2N$-chloric acid, rather less hydrogen is evolved, and more of the acid is reduced to chloride. D. Tommasi found only a trace of hydrochloric acid in chloric acid which has been treated with **aluminium** for six hours; while W. S. Hendrixson found about 20 per cent. of the metal is dissolved by $2N$-chloric acid with the liberation of hydrogen, and the remainder is reduced to chloride. H. Schiff and D. Tommasi stated that iron reduces chlorates; and W. S. Hendrixson found **iron** to dissolve readily in dil. or conc. chloric acid without the evolution of any gas at all, and that iron quantitatively reduces both chloric and bromic acids, so that if iron and sulphuric acid are added to a chlorate or bromate, the reduction to chloride or bromide is complete—the chloride or bromide may be determined by titration with silver nitrate. **Tin,** like iron, passes at once into soln. as stannic chloride, no gas is evolved, and about 99 per cent. of the tin reduces the acid to chloride—very little stannic oxide is formed. A. A. Brochet found that **copper** rapidly dissolves in warm chloric acid forming a blue soln. Copper becomes covered with a crust of cuprous oxide when dipping in cold normal soln. of chloric acid; hence the dissolution of copper is a case of simple oxidation to cuprous oxide which dissolves first as cuprous chloride and chlorate, and is then oxidized to the cupric chloride and chlorate. This suggestion explains how in the electrolysis of soln. of some chlorates with a copper anode, more copper is dissolved at the anode than is deposited on the cathode. Similar remarks apply to cadmium and nickel. Mercury and **antimony** dissolve but slowly in the conc. acid at 70°; bismuth is slowly oxidized, and a portion goes into soln. **Silver** is dissolved by chloric, bromic, or iodic acid, and the acid is reduced according to the equation: $6Ag+6HClO_3=5AgClO_3+AgCl+3H_2O$. The reduction of chloric acid by the metals cannot in all cases be regarded as the effect of nascent hydrogen, but is rather an effect of the tendency of the metal, under the conditions of the experiment, to oxidize at the expense of the oxygen of the acid, or to go into soln. at the expense of the hydrogen which is set free. In the case of iron, tin, and **bismuth,** the preliminary oxidation of the metals is evidenced by the appearance of the oxides—in the case of iron, the oxide dissolves in the excess of acid; with bismuth, the oxide remains undissolved. Arsenic, arsenious acid, and arsenites are oxidized by the chloric, bromic, and iodic acids, or their salts in acid soln.: $3H_3AsO_3+HBrO_3=3H_3AsO_4+HBr$. The conversion of antimonious to antimonic or of arsenious to arsenic salts by a standard soln. of potassium bromate: $KBrO_3+7HCl+3SbCl_3=3H_2O+HBr+KCl+SbCl_5$, is the basis of S. Györy's process for the volumetric determination of antimony[39]—the destruction of the tint of methyl orange by the excess of bromate is utilized for indicating the end of the titration.

The alkali metals and magnesium are attacked in the cold by conc. soln. of iodic acid; aluminium is attacked more slowly; zinc and cadmium are slightly attacked in the cold, rapidly at 100°, disengaging hydrogen and forming iodates; iron dissolves easily in the cold; bismuth is slowly converted by heating into the iodate; copper forms a deposit of cuprous iodate; mercury forms a mixture of iodide and iodate; silver slowly forms iodide and iodate; tin, lead, palladium, gold, and platinum are not attacked by iodic acid. H. Davy's statement that iodic acid dissolves gold and platinum was contradicted by A. Connell and by G. S. Sérullas. The affinity of the metals, potassium, sodium, barium, and silver, said W. Müller-Erzbach, stands in the order named. According to S. Cooke, potassium chlorate

is rapidly reduced by platinum charged with occluded hydrogen; and according to O. Loew and K. Asö, the chlorates and iodates are reduced by platinum black in the presence of glucose. In acid soln. zinc and ferrous sulphate reduce iodates with the separation of iodine, and neutral and alkaline soln. of iodates are reduced to iodides by boiling with zinc dust.

A method of analyzing mixtures of silver bromate or iodate with silver halides was based by A. Purgotti on the property possessed by **potassium hydroxide** or **sodium hydroxide** of attacking the former, and not the latter. C. A. Lobry de Bruyn[40] found that chlorates have no action on **hydroxylamine,** but inflammation occurs if a drop of sulphuric acid is added; iodates are reduced by hydroxylamine. D. Vitali observed that hydroxylamine and phenylhydrazine did not decompose chloric acid, and bromic acid only when heated; iodic acid is reduced in the cold by these reagents. Alkaline soln. of the chlorates are not reduced by **hydrazine sulphate,** but in other soln. the oxidation proceeds: $4(N_2H_4.H_2SO_4)+4O=2N_3H+(NH_4)_2SO_4+3H_2SO_4+4H_2O$, and A. W. Browne and F. F. Shetterley have shown that within certain limits, the yield of azoimide is proportional to the concentration of sulphuric acid, and inversely proportional to the excess of chlorate; the highest yield with potassium chlorate was 22·44 per cent. of N_3H and $48·76NH_3$; with potassium bromate, 6·88 per cent. of N_3H, and 9·77 per cent. of NH_3; and none with potassium iodate. According to M. Schlötter, the reduction of alkali bromates by hydrazine sulphate, $2NaBrO_3+3N_2H_4=2NaBr+6H_2O+3N_2$, enables the bromates to be determined under certain conditions from the volume of nitrogen; the reaction with **hydroxylamine sulphate** is $4NaBrO_3+12NH_2OH=4NaBr+18H_2O+6N_2+3O_2$—some nitrous acid is formed at the same time. E. Rimini symbolizes the reaction between potassium iodate and hydrazine sulphate: $3N_2H_4.H_2SO_4+2KIO_3=3N_2+6H_2O+K_2SO_4+2H_2SO_4+2HI$; followed by $10HI+2KIO_3+H_2SO_4=K_2SO_4+6H_2O+6I_2$; and in alkaline soln.: $3N_2H_4.H_2SO_4+2KIO_3+6KOH=3N_2+2KI+3K_2SO_4+12H_2O$.

According to G. Pellagri,[41] potassium chlorate in aq. soln. is reduced to the chloride by shaking it with iron filings; and H. Eccles noted that it is readily reduced by boiling it with a **copper-zinc couple**—potassium perchlorate is not reduced under similar conditions. Hence, the amount of the one salt can be readily determined when in the presence of the other. On the other hand, J. G. Williams found the perchlorates are reduced by **titanium trichloride,** while the chlorates are not affected. Here again an analytical process is available.

W. Oechsli[42] tried to oxidize chlorates by **ozone,** but obtained no definite results, although T. Fairley claims to have oxidized hypochlorous acid to perchloric acid by ozone. C. W. Bennett and E. L. Mack also established the fact that while the oxidation process is not efficient, it is distinctly in evidence and is favoured by the presence of silver oxide, and it also is carried on by oxygen activated by ultraviolet light. C. F. Schönbein reported that **hydrogen peroxide** does not act on aq. soln. of potassium chlorate or perchlorate;[43] and S. M. Tanatar stated that hydrogen peroxide has no effect on acid or neutral soln. of the chlorates, while the bromates are quickly reduced to bromides, but, according to P. Jannasch and A. Jahn, hydrogen peroxide partially reduces alkaline soln. of the chlorates, and completely reduces the chlorates in dil. nitric acid soln. C. W. Bennett and E. L. Mack obtained no oxidation of hydrogen peroxide in alkaline or neutral soln., but in acid soln. hydrogen peroxide transforms chlorates largely into chlorides, chlorine and chlorine dioxide are set free during the reaction. It is supposed that the chloric acid is reduced to hydrochloric acid in the primary reaction, and this is followed by a secondary reaction: $2HClO_3+2HCl=2H_2O+2ClO_2+Cl_2$. It is assumed that in a dil. soln. of chloric acid, a little chlorine is formed by spontaneous decomposition; this reacts with the hydrogen peroxide, forming hydrochloric acid, which then attacks the remaining chloric acid, forming hydrochloric acid, chlorine, chlorine dioxide, and oxygen. The reaction is thus auto-catalytic, in that a small amount of hydrochloric acid is sufficient to start the reduction. The formation of chlorides

in a soln. of chloric acid and hydrogen peroxide is appreciable at temp. above 80°, in agreement with J. Sand's observation that the velocity of the reaction between hydrochloric and chloric acids is appreciable only at temp. above 70°. With hydrogen peroxide soln. containing less than 0·6 per cent. of iodic acid are slowly decomposed with the separation of iodine: $2HIO_3+5H_2O_2=I_2+6H_2O+5O_2$, with more conc. soln. the separated iodine reacts with the hydrogen peroxide: $I_2+5H_2O=2HIO_3+4H_2O$, so rapidly that the soln. remains colourless.

Chloric acid is oxidized to perchloric acid by **persulphates** in acid solution, and particularly in the presence of traces of silver salts as catalytic agents. Acid solutions of **permanganates** do not oxidize chlorates to perchlorates. A. Purgotti[44] based a method for the analysis of a mixture of silver bromate or iodate with silver halides, on the property possessed by potassium or sodium hydroxide of attacking the former, and not the latter. A. Longi and L. Bonavia find that **sodium peroxide** has no action on iodates or iodides, but it reacts on iodine in dil. soln., forming iodides, and in conc. soln., forming oxyiodides. The different varieties of **carbon** are converted by iodic acid into carbon dioxide; the diamond, however, resists the acid at 250°; wood charcoal is attacked at 160°; sugar charcoal, at 175°; coke and coal, at 180°; anthracite, at 210°; graphite at 240°; amorphous boron is oxidized at 15°; crystalline silicon at 250°. Carbon monoxide is oxidized to the dioxide by iodic acid. When **carbon disulphide** is heated in a sealed tube with iodic acid, it forms iodine and hydriodic acid; and aq. iodates under similar conditions are reduced to iodides.

Iodic acid is distinguished from chloric and bromic acids in the facility with which it forms acid salts. In addition to salts of the type MIO_3, G. S. Sérullas (1830) prepared salts of the type MHI_2O_6, and C. W. Blomstrand (1889) salts of the type $MH_2I_3O_9$. The conductivity and the lowering of the f.p. of soln. of iodic acid, bromic and chloric acids point to the formulæ HIO_3, $HBrO_3$ and $HClO_3$ respectively. This is confirmed by the behaviour of soln. of the corresponding chlorates and iodates.

Uses.—Potassium and barium chlorates are used in the manufacture of fireworks, of safety matches, explosives, etc. Potassium chlorate is used medicinally—especially for gargling the throat in cases of inflammation. Large quantities are poisonous, as is also the case with other potassium salts. The same salt, or the cheaper sodium chlorate, is used as an oxidizing agent and for preparing oxygen in the laboratory. The alkali chlorates are used as an oxidizing agent in the dye industry, and in calico printing. The bromates are also used as oxidizing agents. The so-called *bromine salt*, once recommended as a source of bromine in a process for the extraction of gold, was a mixture of sodium bromide and bromate. Potassium iodate is used in analysis, and the iodates and bromates are used in certain medicinal preparations.

The detection and determination of the chlorates, bromates, and iodates.—*Silver nitrate* gives no precipitate when added to a soln. of a chlorate, but if sulphurous acid be added to the mixture, the chlorate is reduced to a chloride, and a precipitate of silver chloride is formed: $AgClO_3+3H_2SO_3=3H_2SO_4+AgCl$. Cold soln. of bromate form a sparingly soluble white precipitate of silver bromate which dissolves in hot water and ammonia, but is neither dissolved nor decomposed by dil. nitric acid. A similar precipitate of silver iodate is formed in soln. of the iodates. *Mercurous nitrate* gives no precipitate with the chlorates; a white precipitate with bromates; and a pale-yellow precipitate with iodates. Mercurous bromate and iodate are insoluble in dil. nitric acid. Hydrochloric acid converts mercurous bromate into a mixture of mercuric chloride and bromide. *Mercuric chloride* gives a precipitate of mercuric iodate with iodates, but no precipitate with bromates or chlorates. *Copper sulphate* in sulphuric acid soln. gives a precipitate of cuprous iodide with iodates, but no precipitate with chlorates or bromates. *Barium chloride* or *lead nitrate* gives a white precipitate of barium iodate or lead iodate, as the case might be, with the iodates, but not with bromates or chlorates.

A soln. of *potassium permanganate* is not decolorized by chlorates, but it is by the lower oxychlorine compounds. *Diphenylamine sulphate*[46] colours chlorates, bromates, iodates, hypochlorites, or nitrates an intense blue; *brucine* colours a sulphuric acid soln. of chlorates or nitrates orange-red; according to E. Lück the colour disappears on adding stannous chloride. According to G. Denigés, a soln. of *resorcein*[46] (2 grms. in 100 c.c. of water) gives a green coloration with chlorates, but not with bromates. According to R. Böttger, chloric or bromic acid is coloured blue when added to a drop of pure *aniline* previously mixed with 1 c.c. of sulphuric acid- nitrates and iodates give a brownish-red coloration under similar conditions.

Fifteen drops of a mixture of equal volumes of aniline and *o*-toluidine give a dark brown coloration with one drop of a 5 per cent. solution of potassium nitrate; and an intense blood-red coloration with one drop of a one per cent. soln. of potassium chlorate; a blood-red coloration with a 0·1 per cent. soln. of the chlorate; and, on standing 15 minutes, a pale brown coloration with one drop of a 0·01 per cent. soln. of the chlorate.

Chlorates are reduced to a lower state of oxidation by *sulphurous acid*, and the soln. then decolorizes *indigo;* while chloric acid does not decolorize this reagent, *bromic acid does. Ferrous salts in the presence of dil.* sulphuric acid quickly reduce chlorates, but not perchlorates, to chloride: $KClO_3+3H_2SO_4+6FeSO_4 =3Fe_2(SO_4)_3+3H_2O+KCl$.

Chlorates can be determined (1) by reducing the aq. soln. with a Zn-Cu couple: $KClO_3+3H_2=KCl+3H_2O$. Zinc hydroxide formed simultaneously contains some zinc oxychloride. Hence the residue, after filtration and washing, is digested with dil. nitric acid; the zinc precipitated by shaking the soln. with an excess of calcium carbonate; and the clear soln. filtered off. The mixed filtrates contain the chlorine of the chlorate in the form of chloride, and this can be determined in the usual way. (2) Digest the soln. of chlorate with a known amount of stannous *chloride in dil. hydrochloric acid:* $3SnCl_2+KClO_3+6HCl=3SnCl_4+KCl+3H_2O$. The excess of stannous chloride unacted upon by the chlorate can be determined by titration with a standard soln. of potassium permanganate. (3) Sodium hydroxide is added to a soln. of ferrous sulphate; the alkali chlorate is added and all is boiled for a few minutes. The precipitate is dissolved in HCl and titrated with a standard soln. of potassium bichromate to find the amount of ferrous salt. The precipitated ferrous hydroxide is oxidized by the chlorate.

The constitution of chloric, bromic, and iodic acids.—The constitution of chloric acid is by no means clear. Some follow A. Kekulé and W. Odling,[47] and base the graphic formulæ on bivalent oxygen and univalent chlorine. Chloric acid is then represented: $HO-O-O-Cl$. It is known that carbon compounds with chains of oxygen atoms are usually less stable the longer the chain of oxygen. Here, the contrary is the case, HOCl is least stable, and HOOOOCl **is the most stable of the oxy-chlorine acids.** C. W. Blomstrand therefore supposed that the chain formulæ are improbable; the constitution of the oxyhalogen acids can be most satisfactorily explained by assuming that the halogen atom is multivalent, and reaches its maximum septavalency in periodic acid. Accordingly, chlorine monoxide is constituted like nitrogen monoxide, *viz.* Cl—O—Cl; chlorine dioxide, ClO_2 or Cl_2O_4, like nitrogen oxide, namely $O_2\equiv Cl-Cl\equiv O_2$; and chloric acid like nitric acid, namely—

$$HO-Cl\ll^{O}_{O} \qquad HO-Cl<^{O}_{O}$$

where chlorine is respectively represented as quinque- and ter-valent. There is evidence of an isomorphism between chlorates and nitrates. W. Spring assumed that the chlorine atoms in all the chlorine acids have the same function and properties, and accordingly the same valency. He therefore objects to C. W. Blomstrand's suggestion. D. Vorländer, however, rejects A. Kekulé's chain formula, and prefers

C. W. Blomstrand's. H. Stanley argues that the decomposition products of chloric acid favour the formula:

$$H-Cl<\genfrac{}{}{0pt}{}{O}{\dot{O}}>O$$

and says the increasing stability of the oxy-acids is probably connected with the quadrivalency of oxygen. The decomposition of chloric acid into perchloric acid and chlorine dioxide is then represented

$$\underset{\text{Chloric acid.}}{3H-Cl<\genfrac{}{}{0pt}{}{O}{\dot{O}}>O} \rightarrow \underset{\text{Perchloric acid.}}{H-Cl<\genfrac{}{}{0pt}{}{O-O}{O-\dot{O}}} + \underset{\text{Chlorine dioxide.}}{\genfrac{}{}{0pt}{}{O}{\dot{O}}>Cl-Cl<\genfrac{}{}{0pt}{}{O}{\dot{O}}} + H_2O$$

Perchloric acid and its salts are more stable than the chlorates, and yield no chlorine dioxide when heated; they at once evolve oxygen and leave a chloride when heated.

According to H. W. Foote and L. H. Levy, soln. of the alkali chlorates in other molten salts gave f.p. indicating that the mol. wt. under those conditions are normal. A. Rosenheim and O. Liebknecht [48] found the mol. wt. of acid by the f.p. method depend on the concentration, and that the acid in dil. soln. is a monobasic acid, and in conc. soln. the acid is polymerized and exists as a dibasic acid, $H_2I_2O_6$. E. Groschuff and P. Walden also showed that the electrical conductivity of iodic acid soln. corresponds with a monobasic acid, as is also the case with chloric and bromic acids. The monobasic acid, therefore, can be represented by A. Kekulé's type of formula with iodine univalent or C. W. Blomstrand's type of formula, with iodine quinquevalent and iodic anhydride, *i.e.* iodine pentoxide will be represented:

$$\genfrac{}{}{0pt}{}{O}{O}\gg I-O-I\ll\genfrac{}{}{0pt}{}{O}{O}$$

In 1874 J. Thomsen argued that, unlike chloric and bromic acids, iodic acid is dibasic and should be represented by the formula $(HIO_3)_2$, *i.e.* $H_2I_2O_6$, because (i) chloric and bromic acids form very soluble normal salts, never acid salts, while iodic acid forms many sparingly soluble salts, and with the alkalies it forms a series of acid salts, and the anhydride I_2O_5 is easily formed by warming the acid $(HIO_3)_2$. (ii) Iodic acid forms rhombic crystals isomorphous with dibasic succinic acid, $C_2H_4(COOH)_2$, and itaconic acid, $CH_2:C(CH_2COOH)COOH$. (iii) While the heat of formation of the halide acids decreases as the at. wt. of the halogen increases, and the same rule applies to chloric and bromic acid, but with iodic acid, the result is quite different, for its heat of formation, instead of being smaller, is twice as great as that of chloric acid. (iv) If the formula of iodic acid be doubled, and the acid constituted: $I.IO_6H_2$, periodic acid with the formula H_5IO_6 may be regarded as iodic acid with three hydrogen atoms substituted in place of one iodine atom in iodic acid, so as to give $H_3.IO_6H_2$. In 1889, C. W. Blomstrand argued that iodine in iodic acid is quinquevalent, with an oxygen atom and a hydroxyl radicle bound to an IO radicle; and he adapted this hypothesis to the acid and more complex iodates; for example, he represented potassium di-iodate, $KIO_3.HIO_3$, potassium tri-iodate, $KIO_3.2HIO_3$, and potassium molybdamoiodate, $KIO_3.MoO_3$, and C. Friedheim represented potassium sulphatoiodate by the following formulæ:

$$\underset{\text{Potassium di-iodate.}}{\genfrac{}{}{0pt}{}{KO}{O}\gg I<\genfrac{}{}{0pt}{}{O}{O}>I\ll\genfrac{}{}{0pt}{}{OH}{O}} \quad \underset{\text{Potassium tri-iodate.}}{\genfrac{}{}{0pt}{}{KO}{HO}>I\ll\genfrac{}{}{0pt}{}{OO}{O}\gg I<\genfrac{}{}{0pt}{}{OH}{O}I\ll\genfrac{}{}{0pt}{}{O}{O}} \quad \underset{\text{Potassium molybdamo-iodate.}}{\genfrac{}{}{0pt}{}{KO}{O}\gg I<\genfrac{}{}{0pt}{}{O}{O}>Mo\ll\genfrac{}{}{0pt}{}{O}{O}} \quad \underset{\text{Potassium sulphato-iodate.}}{\genfrac{}{}{0pt}{}{KO}{O}\gg I<\genfrac{}{}{0pt}{}{O}{O}>SO<\genfrac{}{}{0pt}{}{OK}{OH}}$$

A. Rosenheim and O. Liebknecht use a similar hypothesis for the simple and complex iodates.

Iodic acid can be regarded as iodine pentoxide, I_2O_5, in which only one oxygen atom is replaced by eq. hydroxyl groups to form $I_2O_4(OH)_2$, or $H_2I_2O_6$, or $2HIO_3$. Acids formed from anhydrides in this way are regarded as meta-acids, so that ordinary iodic acid can

also be called **meta-iodic acid**, and the salts metaiodates; the acid formed by replacing a second oxygen atom by hydroxyl groups is $I_2O_3(OH)_4$, or $H_4I_2O_7$, and is called **dimeso-iodic acid**; the next acid of the series, $I_2O_2(OH)_6$ or H_3IO_4, is **meso-iodic acid**; the next, $I_2O(OH)_8$ or $H_8I_2O_{10}$, is **di-ortho-iodic acid**; and the last of the series, $I_2(OH)_{10}$ or $H_{10}I_2O_{10}$, or $2H_5IO_6$, is **ortho-iodic acid.**

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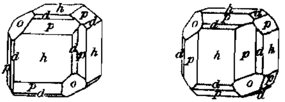
§ 13. The Halogenates—Chlorates, Bromates, and Iodates—of the Metals

Exact observations, guided by the principles of the so-called physical chemistry, have shown that an indefinite number of compounds which have been reported in chemical literature, are mere mixtures.

The chlorates of the different metals are obtained by the action of the acid on the oxide or carbonate; by the action of a sulphate of the desired metal on a soln. of barium chlorate: $Rb_2SO_4+Ba(ClO_3)_2=2RbClO_3+BaSO_4$; or by the general methods previously discussed. Similar remarks apply to the bromates and iodates. *Chlorates* [1] *and iodates* [2] *have been reported in Chili saltpetre, and potassium* iodate in many other varieties of soda and potash nitre, and in mineral phosphates. A. Müntz [3] supposes that the nitrification bacteria in oxidizing the nitrogen also oxidized the iodides. Chloric and bromic acids are monobasic, and each forms a series of **normal salts**: $MClO_3.nH_2O$ or $MBrO_3.nH_2O$ respectively. The iodates are usually less soluble in water than the corresponding chlorates and bromates; and the bromates less soluble than the chlorates. The resemblance between the axial ratios of crystals of silver iodate and nitrate has suggested a possible isomorphism between the nitrates and iodates. The iodates are much more stable than the bromates or chlorates. In addition to the salts of *meta-iodic acid*, $I_2O_4(OH)_2$, *i.e.* $HO.IO_2$, or HIO_3, called normal, iodates, monoiodates, or meta-iodates, G. S. Sérullas [4] has shown that iodic acid, unlike chloric or bromic acid, forms a series of well-defined, stable **acid salts**—the *di-iodates*: $MIO_3.HIO_3.nH_2O$; and the *tri-iodates*: $MIO_3.2HIO_3.nH_2O$—and a number of **complex salts**. The acid salts crystallize from soln. of the normal iodates by the addition of iodic or other acids. Alkali salts of *anhydro-iodic acid*, $H_2I_4O_{11}$, *i.e.* $I_2O_5.2HIO_3$, have been prepared by H. L. Wheeler and H. Landolt; and a copper salt of *dimeso-iodic acid* or *pyro-iodic acid*, $H_4I_2O_7$, has been reported by A. Ditte. R. Rea prepared chlorates of the heavy metals by the decomposition of their sulphates with barium chlorate. He found that the chlorates of zinc, mercury, chromium, iron, copper, and uranium, and the nitrates of zinc, copper, aluminium, and iron are decomposed by hexamethylenetetramine; but the chlorates of nickel, cobalt, magnesinm,

manganese, cadmium, and calcium, as well as the nitrates of nickel, cobalt, magnesium, manganese, and cadmium give addition complexes with that agent. R. Rea found that many of these complex nitrates and chlorates are isomorphous and isodimorphous.

The alkali chlorates.—Lithium chlorate forms deliquescent **crystals** which H. Bruhl [5] observed in three modifications; it also forms a hydrate, $LiClO_3.\frac{1}{2}H_2O$, in plates with twin lamellæ. Sodium chlorate is but very slightly hygroscopic; it usually crystallizes in the cubic system; the crystals are not therefore isomorphous with potassium chlorate. According to H. Copaux,[6] sodium chlorate is tetramorphous, forming: (i) the ordinary cubic form; (ii) unstable rhombic crystals isomorphous with sodium nitrate; (iii) unstable monoclinic crystals isomorphous with potassium chlorate; and (iv) rhombic or pseudo-cubic crystals of low birefringence formed when the salt is crystallized in the presence of sodium sulphate and sodium perchlorate. The cubic crystals separate from the fused salt, and form aq. soln. at ordinary temp., but E. Mallard showed that rhombohedral crystals, very strongly doubly refracting, are obtained from strongly undercooled soln. The effect of various conditions and foreign substances in the soln. of sodium chlorate on the habit of the crystals has been studied by L. Wulff, E. Jacobsen, C. von Hauer, H. von Foullon, and E. Perucca. The last named stained the crystals with sodium or ammonium triphenyltri-*p*-amidodiphenyltolyl carbinol di- (or mono-) sulphonate (extra China blue), and found by ultra-microscopic examination that the dye is not present in the colloidal state; he also studied the effect of the dye on the rotatory power of the crystals, but was unable to find a simple relation between the intensity of the coloration and the rotatory power. The cubic crystals of sodium chlorate are tetartohedral, and, as shown by H. Marbach in 1854, they are optically active, and rotate a ray of polarized light about 6·5 times less than quartz. E. Perucca found the **rotatory power** is not constant with different crystals or with the same crystal at different points or in different directions. The mean value for the *D*-line is $+3·120°$ (13°), and the rotational dispersion, α, at 13° when the wave-length, λ, is expressed in $\mu\mu$ and α in degrees is $\alpha=1168300\lambda^{-2}-0·3514+0·000000306\lambda^2$; T. M. Lowry's formula, $\alpha=a/(\lambda^2-b)$, is not applicable. Both right- and left-handed forms are known. L. Sohncke found the rotation to be 2·38° for the *B*-line; 3·16° for the *D*-line; and the angle increases as the refrangibility of the rays until, as P. A. Guye found, it reaches 14·727° with one of the cadmium lines. The opposite rotations are equal in magnitude but of opposite sign. The right- and left-handed crystals have a mirror-image symmetry. The right-handed crystal of sodium chlorate, Fig. 13, has *h*(100), *p*(210), *d*(110) and *o*(111); and the left-handed crystal, Fig. 14, has *h*(100), *p*(210), *d*(110), and *o*(111). H. Copaux explains the rotary polarization of the cubic crystals by assuming that they are twin-aggregates of the pseudo-cubic form. The rotatory power increases with temp. about 0·00061 per degree. The etching figures on crystals of sodium chlorate are, according to H. Baumhauer, right- and left-handed. F. Pockels has studied the effect of an electrostatic field on the optical activity of the crystals. According to J. Beckenkamp's observations on the **x-radiograms** of sodium chlorate, the structure is similar to that attributed to calcite when the calcium atoms are replaced by sodium, and the carbon atoms by chlorine.



FIGS. 13 and 14.—Right- and Left-handed Crystals of Sodium Chlorate.

Aq. soln. of sodium chlorate are optically inactive no matter whether the soln. be made from the right- or left-handed crystals—presumably because for a state of stable equilibrium—dynamic isomerism—equal quantities of the two isomers are required, and when the aq. soln. of either form is allowed to recrystallize, H. Landolt [7] found equal proportions of the two forms are obtained; but D. Gernez showed that if a right- or left-handed crystal be added to the undercooled soln., only one

kind of crystal, the same as that used for the inoculation, separates from the soln.; F. S. Kipping and W. J. Pope noticed that the presence of a certain quantity of another optically active substance favours the formation of one of the two forms. Potassium chlorate *forms clear or white, colourless, non-hygroscopic crystals belonging to the* monoclinic system[8] in plates or prisms (Fig. 1, Cap. XI), in which the axial ratios are $a : b : c = 0.8331 : 1 : 1.2673$; and $\beta = 109° 42'$. The crystals usually resemble the rhombohedral crystals of calcite, and of sodium nitrate. According to E. Mallard, these crystals are stable up to the m.p., and according to A. Ries, down to very low temp. P. W. Bridgman investigated the effect of press. and temp. on potassium chlorate, and found that under a press. of 5680 kgrm. per sq. cm., a transformation into a second modification occurs at 0°, and the effect of increasing press. on the transition temp. is

Press.	5680	6090	7110	7730	kgrm. per cm.
Transition temp.	0°	40	140	200°	
Change of vol.	0·02510	0·02501	0·02479	0·02466	c.c. per grm.
Latent heat	0·7026	0·8023	0·1050	0·1196	kgrm. m. per grm.

The crystals of rubidium and cæsium chlorates, according to A. Ries and J. W. Retgers, are isomorphous with those of potassium chlorate. J. Herbette has studied the isomorphism of crystals of potassium nitrate and chlorate. Monoclinic crystals with 65 per cent. of chlorate and 35 per cent. of nitrate were obtained, but no rhombic mixed crystals of nitrate and chlorate. Hence, the unstable monoclinic form of the nitrate is isomorphous with the stable form of the chlorate; but no rhombic form of chlorate is isomorphous with the stable rhombic form of the nitrate. Crystals of sodium chlorate are usually *homogeneous, and doubly refracting portions are shown only at low temp.;*[9] R. Brauns induced a temporary double refraction by compressing the crystals. The **index of refraction**[10] of sodium chlorate for the *B*-line is $\mu = 1.51163$; for the *D*-line, $\mu = 1.51267$; and for the Cd-line, $\mu = 1.58500$—at 23°. The **hardness** of potassium chlorate is less than that of rock salt. The **specific gravity**[11] of sodium chlorate is given as 2·289 by C. H. D. Bödeker; 2·490 at 15° by J. W. Retgers, 2·996 by M. le Blanc and P. Rohland; 2·488 by H. Landolt; and 2·467 by M. Berthelot. The sp. gr. of potassium chlorate is 2·326 at 3·9° according to J. P. Joule and L. Playfair; 2·35 at 17·5° (water unity) according to P. Kremers. The extremes of five measurements by H. G. F. Schröder are 2·246 and 2·364.

According to H. W. Foote and L. H. Levy, the **specific heat** of solid sodium chlorate is 0·281, and of the molten salt, 0·581; the latent heat of fusion is 48·5 Cals. per gram. According to H. Kopp,[12] the sp. ht. of potassium chlorate *between 19° and 49° is 0·15631; and according to H. V. Regnault, 0·20956 between* 16° and 98°, and the mol. ht., according to M. Berthelot, is 23·8. According to L. Graetz, the **thermal conductivity** of potassium chlorate at 13° is 0·001153. The **heat of formation**[13] of potassium chlorate from its elements is 95·86 Cals., and of sodium chlorate 84·40 Cals.; the heat of neutralization, $2KOH_{aq.} + Cl_2O_{5aq.} = 27.52$ Cals., and of sodium chlorate, 13·76 Cals.; the heat of the reaction: $3Cl_2 + 6KOH$, =etc. is 97·945 Cals.; the **heat of decomposition:** $4KClO_3 = 3KClO_4 + KCl + 63$ Cals.; and: $KClO_3 = KCl + 3O - 9.77$ Cals., and for sodium chlorate, 12·3 Cals.; the heat of oxidation of potassium chloride in soln. is 15·37 Cals.; the **heat of solution** of sodium chlorate at 10° is −5·57 Cals.; and of potassium chlorate −10·04 Cals., so that the water is cooled when the alkali chlorate is dissolved; and the solubility increases with a rise of temp. E. F. von Stackelberg found the heat of soln. Q of n mol. of potassium chlorate in 100 of water to be $Q = 10500 - 1625n$ cals.

According to H. Bruhl, the **melting point** *of lithium chlorate, $LiClO_3 . \frac{1}{2}H_2O$,* is 63°–65°—A. Potilitzin gives 50°; the molten mass readily forms an undercooled fluid. The hydrate becomes anhydrous in dry air at 90°, and melts at 129°. Lithium chlorate begins to decompose at 270°, and at higher temp. the decomposition is more rapid. The rate of decomposition reaches a maximum with rise of temp.,

and then gradually decreases. This is due to the formation of lithium perchlorate by a side reaction : $4LiClO_3=LiCl+3LiClO_4$ accompanying the direct decomposition, $2LiClO_3=2LiCl+3O_2$. A. Potilitzin also says the perchlorate decomposes $2LiClO_4=LiClO_3+LiCl+O_2$. T. Carnelley gives the m.p. of sodium chlorate as 202° ; J. W. Retgers gives 248° ; A. Smith, 261° ; and H. W. Foote and L. H. Levy, 255°. According to L. Poincaré, fusion commences at 265° without decomposition, but the latter immediately begins if a bubble of gas passes through the fused mass. The decomposition process resembles that of potassium chlorate, but the perchlorate stage is more sharply distinguished, for T. Schlösing showed that the evolution of oxygen completely stops when the fused chlorate has acquired the viscid stage. Potassium chlorate, says J. S. Stas,[14] can be melted in oxygen gas without loss of oxygen, and without decrepitation ; but E. H. Cook says that about 0·03 per cent. of oxygen is lost during the melting of this salt. T. Carnelley gives the m.p. of potassium chlorate as 372 ±2° ; and H. le Chatelier gives 370°. T. Carnelley gives the f.p. as 351°. According to J. J. Pohl, the salt begins to decompose at 352°, and the decomposition is quite rapid.

Unlike soln. of the chlorides, L. Kahlenberg [15] found that the rise of the **boiling point** of soln. containing w grams of potassium chlorate in 100 grms. of water decreased with increasing concentration, being 0·05° for w=8·121 ; 1·31° for w =17·116 ; 2·49° for w=35·42 ; and 3·43° for w=48·92. According to P. Kremers,[16] the sat. soln. of sodium chlorate salt boils at 132°, and by supersaturation, soln. boiling at 135° can be obtained. A sat. soln. of potassium chlorate boils at 105° ; and G. T. Gerlach found that the b.p. of a soln. of potassium chlorate with p grms. of the chlorate per 100 grms. of water, to be

Boiling point .	100°	101°	102	103°	104°	104·4°
Concentration p .	0	13·2	27·8	44·6	62·2	69·2

Solutions with two boiling points.—It has been shown by J. H. van't Hoff [17] that the maximum vap. press., p, of a sat. soln., at the absolute temp. T, can be represented by the relation $d(\log P)/dT=Q/2T^2$, where Q represents the heat of condensation of a kilogram-molecule of the vapour—*i.e.* 18 kilograms of water—to form a sat. soln. The heat of condensation Q is the sum of (i) the heat, q, absorbed when the necessary amount of the sat. soln. is separated into 18 kilograms of water and salt : and (ii) the latent heat of evaporation L of the water. The former quantity is usually negative, and accordingly $Q=L-q$. As a rule, the value of L is large in comparison with q, and the sum is therefore always positive, and the vap. press. of the soln. increases with temp. With some of the very soluble salts—*e.g.* the nitrates of sodium, potassium, silver, thallium, hydrated calcium chloride, etc.—q increases until it is equal to and finally exceeds the value of L. In that case, the vap. press. curve will at first rise rapidly with the temp., then more slowly, and finally will fall with a further rise of temp. This may be established another way. In a closed tube, the vap. press. of a sat. soln., with a rise of temp., increases to a maximum and then falls. This follows from the fact that with a rise of temp., the vap. press, tends to increase, but the solubility of the salt also increases, and this tends to *depress* the vap. press. With the less conc. soln., the latter effect predominates and the pT-curve rises, AB, Fig. 15, until the sat. soln. contains so small a proportion of water that the two opposing tendencies become equal to one another, and afterwards the former effect predominates, and the pT-curve falls, as illustrated diagrammatically, BC, Fig. 15. If a horizontal line MN be drawn at one atm. press., M and N represent the b.p. of sat. soln. one at a much higher temp. and salt concentration than the other. The one OQ is realized by gradually raising the temp. of a sat. soln., and the other OR is realized by cooling

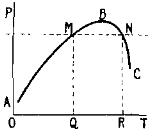


FIG. 15.

the soln. The spitting of silver is an illustration of the second b.p. H. B. Roozeboom and A. Smits have shown that for normal atm. press., with sat. soln. of

	KNO_3	$NaNO_3$	$NaClO_3$	$AgNO_3$	$TlNO_3$
First b.p.	115°	120°	126°	133°	105°
Second b.p.	331°	310°	255°	791°	196°
M.p.	334°	313°	261°	208°	205°

The **solubility** of lithium chlorate in water is perhaps greater than any other known inorganic salt; according to F. Mylius and R. Funk,[18] 100 grms. of water at 18° *dissolve 313·5 grms. of lithium chlorate—the molecular proportions are* $LiClO_3 + 1{\cdot}6H_2O$ and this soln. contains 75·8 per cent. of the salt, and has a sp. gr. of 1·815. The hemihydrate, $LiClO_3.\frac{1}{2}H_2O$, was obtained by A. Potilitzin by evaporation of the aq. soln. over sulphuric acid; the evidence, however, in favour of the existence of the hydrate is not accepted by all. According to P. Kremers, the solubility of sodium chlorate referred to the stable cubic form, and expressed as (*a*) parts of salt per 100 parts of water; and (*b*) per cent. of salt is

	0°	12°	20°	40°	60°	80°	100°	120°
a	81·9	89·3	99·0	123·5	147·1	175·6	232·6	333·3
b	45·0	47·2	49·7	55·3	59·5	63·7	69·9	76·9

The solubility of potassium chlorate in water has been determined by G. J. Mulder, J. L. Gay Lussac, C. A. Gerardin, L. Tschugaeff and W. Chlopin, and B. Pawlewsky.[19] The latter found (*a*) the percentage amount of potassium chlorate in the sat. soln.; and (*b*) the amount of the salt dissolved by 100 parts of water:

	0°	10°	20°	30°	40°	50°	60°	80°	100°
a .	3·06	4·27	6·76	8·46	11·75	15·18	18·97	26·97	35·83
b .	3·14	4·45	7·22	9·26	13·31	17·95	23·42	36·33	55·54

Above 50°, the solubility thus increases rapidly with the rise of temp. The solubility at 120° is 35·83 per cent.; at 120°, 42·4; at 190°, 69·7; and at 330°, 96·7 per cent. A. Étard represents the solubility of potassium chlorate S, at a temp. θ between 0° and 42° by $S=2{\cdot}6+0{\cdot}2000\theta$; between 42° and 171° by $S=11{\cdot}0+0{\cdot}3706\theta$; and between 171° and 359°, by $S=59{\cdot}0+0{\cdot}2186\theta$; and C. Blarez finds that the amount of potassium chlorate in 100 grms. of water between 0° and 30° is given by $S=3{\cdot}2+0{\cdot}109\theta+0{\cdot}0043\theta^2$; and N. G. Nordenskjöld gives between 0° and 105° $\log S=0{\cdot}5224+0{\cdot}0178340\theta-0{\cdot}0000555\theta^2$. W. Reissig found the solubility of rubidium chlorate in 100 parts of water to be 2·8 at 4·7°; 3·9 at 13°; 4·9 at 18·2°; and 5·1 at 19°. F. Calzolari found the solubilities of cæsium chlorate and perchlorate at 20° to be somewhat less than the corresponding potassium salts, but more than those of rubidium. The order of solubilities varies with temp. He does not consider these observations agree with the predictions based on the theory of electro-affinity. His values for the three chlorates expressed in grams of salt per 100 grms. of water are:

	0°	8°	19·8°	30°	42·2°	49·08°	74·9°	99°
$KClO_3$ . .	3·30	4·48	7·15	10·27	—	18·96	35·40	57·3
$RbClO_3$ . .	2·138	3·07	5·36	8·00	12·48	15·98 (50°)	34·12 (76°)	62·8
$CsClO_3$ . .	2·46	3·50	6·28	9·53	14·94	19·40 (50°)	41·65 (77°)	76·5

The solubility of potassium chlorate is depressed by the addition of other potassium salts, or by the addition of other chlorates; F. Winteler, and T. Schlösing have measured the solubility of potassium chlorate in *potassium chloride* soln. and of sodium chlorate in soln. of *sodium chloride*. In accord with the general rule, the solubility is diminished by the addition of a salt with a common ion. S. Arrhenius measured the solubility of potassium chlorate in aq. soln. of *potassium nitrate*; and C. Blarez in aq. soln. of *potassium bromide, chloride, iodide, nitrate, sulphate, oxalate, and hydroxide*; H. T. Calvert, and J. N. Brönsted in an aq soln. of the last-named compound. H. T. Calvert also measured the solubility of potassium

chlorate in *hydrogen peroxide*. Potassium chlorate dissolves in soln. of *ammonium nitrate* or *acetic acid* more copiously than in water; and less copiously in soln. of dil. hydrochloric acid, nitric acid, ammonium acetate, and aq. ammonia. The passing of *ammonia* into an aq. soln. of potassium chlorate precipitates the salt. According to D. P. Konowaloff, a 5·2 per cent. soln. of ammonia dissolved 52·5 grms. of potassium chlorate. T. W. B. Welsh and H. J. Broderson found that 100 c.c. of anhydrous *hydrazine* dissolve 66 grms. of sodium chlorate at ordinary temp.

Lithium chlorate is very soluble in *alcohol;* the chlorates of the other alkalies having a low solubility in this menstruum. Potassium chlorate is precipitated from its aq. soln. by the addition of alcohol or acetone. The solubility of potassium chlorate[20] in absolute alcohol, *acetone, ether*, and *chloroform* is virtually nil, and in aq. alcohol or acetone, at a constant temp., the solubility increases as the proportion of water increases. For example, at 30° the number of grams of potassium chlorate which are dissolved in 100 grms. (*a*) of soln., (*b*) of water when the solvent contains *p* per cent. of alcohol:

p		0	5	10	20	30	50	70	90
$KClO_3$	Soln.	9·23	7·72	6·44	4·51	3·21	1·64	0·54	0·06
	Water	10·17	8·80	7·65	5·90	4·74	3·33	1·82	0·62

A. Wächter and G. C. Wittstein have shown that the solubility of sodium chlorate is also much smaller in alcohol than in water. 100 grms. of alcohol dissolve one gram of sodium chlorate at 25°, and 2·5 grms. at the b.p.; 100 grms. of a 77 per cent. soln. of alcohol at 16°, dissolve 2·94 grms. of sodium chlorate. Similarly aq. *acetone*, at 30°, dissolves the following amounts of potassium chlorate:

p		0	5	10	20	30	50	70	90
$KClO_3$	Soln.	9·23	8·32	7·63	6·09	4·93	2·90	1·24	0·18
	Water	10·17	9·55	9·09	8·10	7·40	5·98	4·18	1·82

A. M. Ossendowsky found that at 15·5°, 100 grms. of *glycerol* dissolve 3·5 grms. of potassium chlorate, or 20 grms. of sodium chlorate. According to W. O. de Coninck, 100 grms. of a sat. soln. in *glycol* contain 0·9 grm. of potassium chlorate. Liquid *hydrogen chloride* becomes yellow in contact with potassium chlorate without dissolving any appreciable quantity. Sodium chlorate and bromate dissolve easily in *liquid ammonia*.[21] F. Ephraim found that the **lithium tetrammino-chlorate** forms a fairly mobile liquid. J. N. Brönsted obtained 2020 cals. for the affinity of the reaction $KCl+NaClO_3 \rightarrow KClO_3+NaCl$ at 16·39°.

G. T. Gerlach has calculated the **specific gravities** of soln. of sodium chlorate at 19·5°, from P. Kremers' data,[22] and found

Per cent. $NaClO_3$	10	15	20	25	30	35
Sp. gr.	1·070	1·108	1·147	1·190	1·235	1·282

The corresponding sp. gr. of soln. of potassium chlorate are

Per cent. $KClO_3$	1	2	4	6	8	10
Sp. gr.	1·007	1·014	1·026	1·039	1·052	1·066

B. Carlson also measured the sp. gr. of aq. soln. of the alkali chlorates; W. Schmidt[23] measured the **compressibility** of aq. soln. of potassium chlorate at 17°, and found that soln. of sp. gr. 1·009, 0·193, 1·024 respectively had the compressibility coeff., β, 0·0000454, 0·0000429, and 0·0000409. The **freezing point** is lowered 0·215° by the addition of a gram of potassium chlorate to 100 grms. of water. H. Jahn[24] represented the f.p. of soln. containing n mol. of potassium per 1000 grms. of water by $3·5690n-2·3067n^2$; and for sodium chlorate, $3·5812n-1·3040n^2$. The **vapour pressure** of a soln. of a gram of potassium chlorate in 100 grms. of water is lowered $0·240\times7·6$. G. Tammann found the vap. press. of a soln. of 3·92 grms. of potassium in 100 grms. of water lowered the

vap. press. of water 7·0 mm., and 50·60 grms., 82·4 mm.; with sodium chlorate, 9·02 grms. lowered the vap. press. 19·7 mm., and 160·16 grms. lowered it 290 mm. R. Abegg and H. Riesenfeld found the partial press. of normal soln. of potassium chlorate to be 14·51 mm..

E. Doumer[25] gives the index of refraction of dil. soln. of potassium chlorate μ=0·155; and $M\mu$=19·0 for sodium chlorate. M. le Blanc and P. Rohland give the index of refraction 1·5145 and sp. gr. 2·496, making the molecular refraction 21·96 by Gladstone and Dale's formula, and 12·86 by Lorentz and Lorenz's formula. H. A. Miers and F. Isaac measured the **indices of refraction** of crystallizing soln. of sodium chlorate. A 55·77 per cent. soln. at 53·5° had an index of refraction 1·39125; and a 51·035 per cent. soln. at 43·5°, an index of refraction of 1·387083. When crystals of potassium chlorate are rubbed in darkness they show a transient luminescence—**triboluminescence.** According to G. Foussereau,[26] the **electrical conductivity** of crystals of potassium chlorate per cm. cube is $0·268\times10^{-12}$ reciprocal ohms at 145°; $0·125\times10^{-4}$ at 352°; and for the molten solid at 359°, 0·238 reciprocal ohms. The eq. conductivities of soln. of the chlorates[27] at a dilution one mol. of the salt per v litres, at 25°, are as follows:

v	2	8	32	128	512	1024	2048
$\lambda LiClO_3$	—	—	91·5	96·8	100·4	101·5	—
$\lambda NaClO_3$	74·7	86·7	95·0	101·1	104·6	104·1	104·1
$\lambda KClO_3$	—	104·7	115·2	122·8	126·1	127·8	128·4

The **temperature coefficients** of the conductivities of the sodium and potassium salts were given by H. C. Jones; so also the **ionization constants,** α. The latter, at 25°, were

$\alpha NaClO_3$	71·4	82·9	90·8	96·6	100·0	—	
$\alpha KClO_3$	—	79·7	87·5	95·2	95·9	97·2	97·7

W. Hittorf's **transport number** for the anion ClO_3' in a 0·3N-soln. is 0·445; and 0·462 in a 0·07N-soln.

The alkali bromates.—According to C. F. Rammelsberg,[28] **lithium bromate,** $LiBrO_3$, is obtained in needle-like crystals by evaporating an aq. soln. in vacuo over sulphuric acid. A. Potilitzin says the crystals are rhombic pyramids with a molecule of water of crystallization, F. Mylius and R. Funk say the salt is probably anhydrous. Crystals of **sodium bromate,** $NaBrO_3$, were prepared by C. Löwig and by E. Mitscherlich, who noted their resemblance to sodium chlorate. The crystals of sodium bromate are isomorphous with those of the chlorate, and the two salts form mixed crystals. In 1855, H. Marbach[29] found enantiomorphic crystals which exhibited circular polarization; the bromate like the chlorate is optically active, and H. Traube found that a crystal of sodium bromate, a millimetre thick, rotated the plane of polarized D-light, 2° 10′. J. W. Retgers, and R. Brauns found the crystals of sodium bromate to be trimorphous—(i) cubic tetartohedral crystals; (ii) rhombohedral; and (iii) rhombic. A. J. Balard obtained needle-like crystals by the cooling of hot soln., and C. Löwig, by the very slow cooling of hot soln. obtained 4- or 6-sided plates, or pseudo-cubic crystals. H. and W. Biltz prepare potassium bromate as follows:

Run 80 grms. of bromine slowly, drop by drop, into a soln. of 62 grms. of potassium hydroxide in an equal weight of water. The soln. acquires a yellow colour, and a crystalline powder of potassium bromate is deposited when the soln. cools. The crystals are collected on a Buchner's funnel, and purified by recrystallization from 130 c.c. of boiling water. Potassium bromide is recovered from the mother liquor and washings by evaporation to dryness, admixture with charcoal, calcination, etc.

The crystals of potassium bromate were at first thought to be cubic, but C. F. Rammelsberg[30] showed that they are pseudo-cubic and belong to the trigonal system, where $a:c=1:1·3572$, and α=85° 57′. They are isodimorphous with potassium chlorate in that the two salts form trigonal mixed crystals if the bromate is in

excess and monoclinic crystals if the chlorate is in excess. There is an intervening lacuna. H. Marbach found the crystals to show negative double refraction.

The crystals of sodium bromate prepared by P. Kremers had a **specific gravity** 3·339 with respect to water at 17·5°; and by M. le Blanc and P. Rohland, 3·254. Similarly P. Kremers [31] found the crystals of potassium bromate had a sp. gr. 3·271 at 17·5°; and H. Topsöe, 3·218. The **heat of formation** of potassium bromate from its elements is 84·1 Cals. (J. Thomsen) and 84·3 Cals. (M. Berthelot); the **heat of solution** of potassium bromate in 200 mol. of water is −9·76 Cals. (J. Thomsen), in 400 mol. of water −9·76 (M. Berthelot), and in 460 mol. of water at 11°, −9·85 Cals. E. F. von Stackelberg gives for the heat of soln. Q of n mol. of potassium bromate in 100 of water: Q=10200−1400n cals. The **heat of neutralization**: $HBrO_3$+NaOH+aq.=13·78 Cals.[32] The **heat of decomposition**: $KBrO_3$→KBr+3O+11·1 Cals. The crystals of sodium bromate, according to T. Carnelley and W. C. Williams,[33] have a m.p. 381°±6°. Potassium bromate does not alter when heated up to 180°; it then decrepitates and melts at 370°, giving off, according to E. H. Cook, a little bromine, −0·08 per cent. The alkali bromates decompose when heated into the alkali bromide and oxygen; there is no evidence of the formation of any perbromate. A. Potilitzin found potassium bromate lost 0·45 per cent. when heated 2-3 hrs. at 300°; 4 per cent. in 30 minutes at the m.p. 370°. When heated very slowly no bromine was obtained although three-fourths of the available oxygen had been expelled.

According to P. Kremers, a sat. soln. of sodium bromate has a **boiling point** 109°; potassium bromate, 104°, and if supersaturated, 106°. H. Jahn [34] represents the lowering of the **freezing point** of 0·1 to 0·3N-soln. of sodium bromate by 3·5669N−1·4806N^2, and for 0·12 to 0·026N-soln. of potassium bromate by 3·5635N−2·0446N^2. For the more dil. soln. the **degree of ionization** calculated from the depression of the f.p. agrees with the law of mass action. G. Tammann found the lowering of the **vapour pressure** of water from its value at 100° by the soln. of 9·57 grms. of sodium bromate in 100 grms. of water to be 15·5 mm.; 84·23 grms., 150·2 mm.; and with 6·59 grms. of potassium bromate, 8·4 mm., and 38·91 grms., 51·9 mm. R. Abegg and H. Riesenfeld found the partial press. of N-soln. of *ammonia* with $\frac{1}{4}N$-soln. of potassium bromate is 14·31 mm. at 25°. F. Mylius and R. Funk [35] say that 100 grms. of water at 18° dissolve 153·7 grms. of the lithium bromate, and the soln. contains 60·4 per cent. $LiBrO_3$ of sp. gr. 1·833. According to P. Kremers, 100 grms. of *water* dissolve:

	0°	20°	40°	60°	80°	100°
Grms. $NaBrO_3$.	27·54	34·48	50·25	62·5	75·75	90·9
Grms. $KBrO_3$.	3·11	6·92	13·24	22·76	33·90	49·75

The soln. are readily under-cooled. According to C. Löwig, aq. soln. of the sodium bromate below 4° deposit crystals of the hydrated salt. The solubility data for potassium bromate are due to J. J. Pohl.[36] The solubilities of potassium bromate in soln. of *sodium nitrate* and of *sodium chloride* were determined by G. Geffcken. V. Rothmund measured the solubility of potassium bromate in grams per litre, at 25°, in half normal aq. soln. of *methyl alcohol*, 74·16; *ethyl alcohol*, 70·33; *propyl alcohol*, 70·33; *tertiary amyl alcohol*, 63·97; *acetone*, 70·99; *ethyl ether*, 65·98; *formaldehyde*, 66·31; *glycol*, 75·34; *mannitol*, 75·34; *grape sugar*, 71·99; *urea*, 79·68; *dimethylpyrone*, 79·84; *ammonia*, 74·33; *dimethylamine*, 64·13; *pyridine*, 69·31; *piperidine*, 66·15; *urethane*, 72·33; *formamide*, 79·02; *acetamide*, 74·33; *glycocol*, 83·68; *acetic acid*, 76·17; *phenol*, 71·15; *methylal*, 67·66; and *methyl acetate*, 70·151.

J. C. G. de Marignac [37] reported the formation of a double compound of sodium bromide and bromate by saturating a soln. of sodium hydroxide with bromine, and driving off the excess by heat. The mother liquid deposits long needle-like monoclinic crystals. According to J. C. G. de Marignac, the crystals have the composition $NaBr.2NaBrO_3.2H_2O$; and according to C. Fritzsche, $2NaBr.3NaBrO_3.3H_2O$. Water or alcohol extracts sodium bromate from the crystals.

The **specific gravity of solutions** of potassium bromate, calculated by G. T. Gerlach [38] from P. Kremers' data at 19·5°,

Per cent. $KBrO_3$	1	2	3	4	5	6	7	8	9	10
Sp. gr.	1·009	1·016	1·024	1·031	1·039	1·046	1·054	1·062	1·070	1·079

For sodium bromate the numbers are :

Per cent. $NaBrO_3$	5	10	15	20	25	30
Sp. gr.	1·041	1·083	1·129	1·178	1·231	1·289

The index of refraction of dil. soln. of sodium bromate [39] is $\mu=0·131$; $M\mu=20·7$. Sodium bromate crystals have the **index of refraction** 1·5943, sp. gr. 3·254 ; the **molecular refraction** by Gladstone and Dale's formula is therefore 27·58 ; and by Lorentz and Lorenz's formula 15·75. The eq. conductivity of soln. of potassium bromate at 25° change from 114·4, with a mol. per 32 litres, to 126·3, with a mol. per 1024 litres.[40]

The alkali iodates.—A. A. Hayes [41] reported the occurrence of native sodium iodate accompanying the calcium borate near Iquique. Anhydrous **lithium iodate,** $LiIO_3$, was prepared by C. F. Rammelsberg in 1838, and in 1897 by F. Mylius and R. Funk, by neutralizing lithium carbonate or hydroxide with iodic acid. The corresponding **sodium iodate,** $NaIO_3$, was prepared by J. von Liebig [42] by saturating water containing finely divided iodine in suspension by means of chlorine gas, neutralizing the liquid with sodium carbonate ; and after again passing chlorine gas until the iodine is all dissolved, again neutralizing with sodium carbonate. The soln. was evaporated to about one-tenth its volume, mixed with half its volume of alcohol, and the sodium chloride washed from the precipitate by means of alcohol. The sodium carbonate was removed by treatment with acetic acid, and the sodium acetate washed out with alcohol. Similar remarks apply for **potassium iodate,** KIO_3. According to G. Magnus and F. Ammermüller, if an excess of sodium carbonate be employed, sodium periodate is formed ; the sodium iodate, said A. Duflos, can be separated from the chloride by crystallization, without the alcohol treatment. G. S. Sérullas employed a somewhat analogous process with an aq. soln. of iodine chloride in place of chlorine and iodine. A. Longi and L. Bonavia oxidized sodium iodide soln. with hydrogen peroxide ; and E. Péchard reduced sodium periodate soln. with sodium iodide. Similarly potassium iodate, KIO_3, was made by J. L. Gay Lussac [43] by the action of iodine on hot potash lye, and after concentrating the soln., precipitating the iodate by the addition of alcohol. N. A. E. Millon made it by neutralizing potassium hydroxide or carbonate with iodic acid ; W. Stevenson by treating a soln. of barium iodate with potassium sulphate ; O. Henry, and also J. S. Stas, by melting together an intimate mixture of potassium iodide and chlorate up to the temp. at which the chlorate begins to decompose. The iodate and chloride are readily separated by fractional crystallization ; J. S. Stas also made it by heating iodine with potassium chlorate. The oxidation of iodine by potassium chlorate can be conducted somewhat as follows :

Dissolve 30 grms. of potassium chlorate in 60 c.c. of warm water contained in a 250 c.c. flask. Add 35 grms of iodine, and then 2 c.c. of conc. nitric acid. A vigorous reaction sets in ; chlorine gas along with a little vapour of iodine escapes. When the reaction subsides, boil the liquid to drive off the dissolved chlorine, and then add another gram of iodine. Concentrate the soln. by evaporation, and collect the crystals of potassium iodate on a Buchner's funnel. The crude product is purified by dissolving it in about 150 c.c. of hot water, neutralize the soln. with potassium hydroxide, and on cooling crystals of the desired salt are obtained.

L. Henry passed chlorine into water containing finely divided iodine in suspension until all was dissolved ; he then added a mol. of potassium chlorate per gram-atom of iodine in soln. Potassium iodate was formed when the liquid warmed, and chlorine was copiously evolved: $KClO_3+ICl=KIO_3+Cl_2$. L. P. de St. Giles used a soln. of potassium permanganate to oxidize potassium iodide: $2KMnO_4$

$+KI+H_2O=2MnO_2+2KOH+KIO_3$; or iodine: $10KMnO_4+3I_2+2H_2O=10MnO_2+4KOH+6KIO_3$. The equation: $KI+2KMnO_4=KIO_3+K_2Mn_2O_5$, is sometimes used to represent the oxidation. The process is illustrated by H. Erdmann's method of preparation:

A soln. of 20 grms. of potassium iodide, in a small proportion of water, is poured into a hot soln. of 40 grms. of potassium permanganate in a litre of water. The mixture is heated on a water bath for about half-an-hour, and alcohol is added, drop by drop, to the pink soln. until the permanganate is decolorized. Filter the mixture, and wash the precipitate which is probably potassium manganite. Just acidify the alkaline filtrate with acetic acid, and evaporate the liquid down to about 50 c.c. The mother liquor is poured from the granular crystals of potassium iodate which separate as the soln. cools, the crystals are washed repeatedly with absolute alcohol, and dried. About 25 grms. of potassium iodate are so obtained.

E. Müller made potassium iodate by electrolyzing the iodide. H. L. Wheeler[44] made rubidium iodate, $RbIO_3$, by the action of a mol. of iodine pentoxide on one of rubidium carbonate; by treating a hot dil. soln. of iodine trichloride with rubidium hydroxide or carbonate; by the action of iodic acid on a hot conc. soln. of rubidium chloride, RbCl. T. V. Barker obtained a good yield by passing chlorine into a hot conc. soln. of a mixture of rubidium iodide and hydroxide whereby the sparingly soluble iodate is precipitated. Cæsium iodate, $CsIO_3$, was made in a similar way.

A. Ditte[45] prepared **crystals** of sodium iodate by dissolving the salt in warm sulphuric acid dil. with half its volume of water; and evaporating over conc. sulphuric acid. Colourless strongly double refracting, rhombic crystals are formed: $a:b:c=0.9046:1:1.2815$. The crystals of sodium iodate, says A. S. Eakle, form isomorphous mixtures with ammonium iodate. According to T. V. Barker, the crystals of the iodates of potassium, rubidium, and cæsium form an isomorphous group crystallizing in what appear to be cubes, but which are really made up of four monoclinic sub-individuals, interpenetratingly twinned. The axial ratios for potassium iodate are $a:b:c=1.0089:1:1.4394$; $\beta=90°\ 15'$. The crystals of the iodate are not isomorphous with the chlorate and bromate, and according to A. Ries, the iodate and chlorate do not form mixed crystals.

The **specific gravity** of the crystals of sodium iodate is 4·277 (P. Kremers),[46] potassium iodate, 3·979 at 17·5° (P. Kremers), 2·601 (A. Ditte). The sp. gr. of rubidium iodate is 4·559 at 14° (water at 4° unity), and similarly for cæsium iodate, 4·831 at 16° (water at 4° unity)—the corresponding mol. vol. are respectively 57·14 and 63·68. The **heat of formation** of potassium iodate from its elements is 124·49 Cals. (J. Thomsen) and 123·9 (M. Berthelot); if the iodine is gaseous, 129·36 Cals. (M. Berthelot).[47] The **heat of neutralization**: $KOH_{aq.}+HIO_{3aq.}=13.81$ Cals.; the **heat of solution** of an eq. of potassium iodate in a litre of water at 13° is 14·3 Cals.; in 4 litres of water, 14·25 Cals. The heat of soln. of potassium iodate is −6·78 Cals.; for a grm. of potassium iodate in 40 grms. of water at 12°, −6·05 Cals.; the heat of dil. of a soln. of an eq. of potassium iodate in 2 litres of water, with two more litres of water at 13° is −0·36 Cal. E. F. von Stackelberg gives for the heat of soln., Q, of n mol. of potassium iodate in 100 mol. of water: $Q=7000-1900n$ Cals. The **heat of decomposition,** $KIO_3=KI+3O-44.1$ (M. Berthelot), −44·36 (J. Thomsen). When sodium iodate is heated oxygen is given off, and an iodide with an alkaline reaction is formed, showing that some iodine is lost as well as oxygen;[48] and J. L. Gay Lussac found a complex residue remained owing to the loss of iodine when sodium iodate is kept in a state of fusion for some time.

The **melting point** of potassium iodate[49] is 560°±1°. As J. L. Gay Lussac showed in 1814, the iodate decomposes into oxygen and potassium iodide at a higher temp. than the chlorate. According to E. H. Cook, some iodine is lost at the same time. According to G. F. Rammelsberg, no periodate is formed. The reaction is catalyzed by pyrolusite as in the analogous chlorate reaction. The **boiling point** of a sat. soln. of sodium iodate is 102° (P. Kremers),[50] 105° (A. Ditte),

and of potassium iodate, 102°. H. Jahn found the lowering of the **freezing point** for 0·12 to 0·026*N*-soln. of potassium iodate is $3·5614N-2·7357N^2$, and in dil. soln. the degree of ionization calculated from the depression of the f.p. is in accord with the mass law. R. Abegg and H. Riesenfeld say that the partial press. of a normal soln. of *ammonia* with ½*N*-potassium iodate is 14·14 mm. at 25°. Lithium iodate, said C. F. Rammelsberg, is soluble in about twice its weight of cold *water*, and in very little more hot water; and according to F. Mylius and R. Funk, 100 grms. of water at 18°, dissolve 80·3 grms. of the salt, and the soln. then contains 44·6 per cent. of $LiIO_3$, and its sp. gr. is 1·568. According to P. Kremers,[51] the solubility of sodium iodate in 100 grms. of water is

	0°	20°	40°	60°	80°	100°
$NaIO_3$	2·5	9·0	15·0	21·0	27·0	34·0 grms.
KIO_3	4·73	8·13	12·8	18·5	24·8	32·2 ,,

Sodium iodate dissolves copiously in warm dil. sulphuric acid without decomposition; but it is decomposed by hydrochloric acid. The presence of *potassium iodide* causes potassium iodate to dissolve more readily than in pure water; and although A. Ditte says that a double salt is not obtained from the soln., yet the phenomenon is probably due to the formation of a complex salt in soln. J. N. Brönsted measured the solubility of potassium iodate in aq. soln. of potassium hydroxide. Potassium iodate does not dissolve in alcohol. According to H. L. Wheeler, 100 grms. of water at 23° dissolve 2·1 grms. of rubidium iodate, and 2·6 grms. of cæsium iodate at 24°. The **specific gravity** of a sat. aq. soln. of lithium iodate [52] at 18° is 1·568; the sp. gr. of soln. of potassium iodate calculated by G. T. Gerlach from P. Kremers' data, are:

Per cent. KIO_3 . .	1	2	3	4	5	6	7	8	9	10
Sp. gr. . .	1·010	1·019	1·027	1·035	1·044	1·052	1·061	1·071	1·080	1·090

The **index of refraction** [53] of dil. soln. of potassium iodate is $\mu=0·106$, and the **molecular refraction** $M\mu=22·8$. The eq. conductivities [54] of the iodates are:

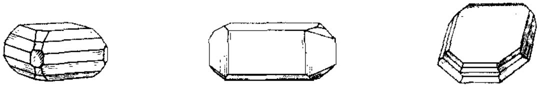
v	32	64	128	256	512	1024
$LiIO_3$	91·5	94·2	96·8	99·4	100·4	101·5
$NaIO_3$	79·3	82·4	85·0	87·1	88·8	90·2
KIO_3	100·8	104·4	107·4	109·7	111·5	112 7

The **degree of ionization** of soln. with 0·0001 mol. of potassium iodate per litre is 99·1 per cent.; 0·001 mol. per litre, 97·5; 0·01 mol. per litre, 92·6; 0·1 mol. per litre, 80·9, and 0·2 mol. per litre, 75·5 per cent. G. N. Lewis and G. A. Linhart have compared the degrees of ionization of sodium and potassium iodates calculated from the ratios λ/λ_∞ measured by A. A. Noyes and G. K. Falk with those computed thermodynamically, and found the latter about 5 per cent. less than the former.

Hydrated alkali iodates.—According to A. Ditte,[55] *Recherches sur l'acide iodique* (Paris, (1870), a neutral soln. of iodic acid in lithium hydroxide furnishes needle-like crystals when slowly evaporated at 60°. The crystals are regarded as **monohydrated lithium iodate,** $LiIO_3.H_2O$; and are said to lose their water of crystallization at 180°. The crystals deliquesce in air; they are very soluble in water; and when treated with dil. sulphuric acid, give crystals of hydrated iodic acid. Sodium iodate crystals have been reported with 1, 1½, 2, 3, 5, 6, and 8 molecules of water of crystallization. The limits of temp. and the conditions of equilibrium of these different hydrates have not been investigated by modern methods. According to A. Ditte, the **monohydrated sodium iodate,** $NaIO_3.H_2O$, separates between 50° and 105° from a soln. of sodium iodate, sat. at its b.p., or by mixing the soln. with alcohol. The best crystals are formed in a slightly alkaline soln. The water is lost over conc. sulphuric acid. The **sesquihydrated sodium iodate,** $NaIO_3.1\frac{1}{2}H_2O$, is said by A. Ditte to separate in fine needles from a hot sat. soln. between 28° and 40°; or by drying the pentahydrate at 30°. P. A. Meerburg obtained confirmatory evidence of the existence of this hydrate at 30°—Fig. 20. If a strongly alkaline soln. of sodium iodate be evaporated between 24° and 28°,

dihydrated sodium iodate, $NaIO_3.2H_2O$, is formed in long prismatic crystals. Other hydrates are transformed into these same crystals if heated with the soln. for a day between 24° and 28°. F. Penny and N. A. E. Millon claimed to have obtained octahedral crystals of **trihydrated sodium iodate,** $NaIO_3.3H_2O$, by cooling a dil. soln. of sodium iodate at 20°. The crystals effloresce in air. A. Ditte[56] also prepared fine needle-like rhombic crystals of **pentahydrated sodium iodate,** $NaIO_3.5H_2O$, by rapidly cooling conc. soln. between −2° and −22°, or by slowly evaporating soln. of sodium iodate at about −2°. The crystals effloresce in dry air, forming crystals of the sesquihydrate. N. A. E. Millon claimed to have produced a **hexahydrated sodium iodate,** $NaIO_3.6H_2O$, by keeping the octahydrate under a bell jar at 0° until the weight was constant; and **octahydrated sodium iodate,** $NaIO_3.8H_2O$, by allowing the iodate to crystallize at 10°, and keeping the product in salt water at 0°. The crystals of the octahydrate lose their water very rapidly. A. Ditte reported the formation of rhombic crystals of the **hemihydrated potassium iodate,** $KIO_3.\frac{1}{2}H_2O$, by the slow evaporation of a dil. sulphuric acid soln. of potassium iodate. These crystals melt when heated, and lose their water of crystallization at 190°. P. A. Meerburg could not find this hydrate in his study of the ternary system, $KIO_3-HIO_3-H_2O$, at 30°.

Acid alkali iodates.—The ternary system, $KIO_3-HIO_3-H_2O$, can give the monoiodate, KIO_3; the di-iodate, $KIO_3.HIO_3$; and the tri-iodate, $KIO_3.2HIO_3$. The anhydrous salt can unite with iodic acid, forming readily crystallizable salts, and the anhydrous salts, $KIO_3.HIO_3$ and $KIO_3.2HIO_3$, have been described by G. S. Sérullas and N. A. E. Millon. The tri-iodate was considered by C. F. Rammelsberg and F. Penny to contain some water of crystallization, but this view is wrong,



FIGS. 16 to 18.—Trimorphism of Potassium Di-iodate, $KIO_3.HIO_3$.

for P. A. Meerburg found none. The crystalline constants of these salts have been described by J. C. G. de Marignac, C. F. Rammelsberg, and J. Schabus.

G. S. Sérullas made **potassium di-iodate** by adding alcohol to a soln. of the normal iodate in dil. hydrochloric acid; and also by crystallization from a soln. of the double salt of potassium chloride and iodate in much water at 25°; N. A. E. Millon and A. Ditte, by treating iodic acid with half the amount of potassium hydroxide required for complete neutralization; A. Ditte, by slowly cooling a soln. of the normal iodate in dil. nitric acid; and N. A. E. Millon, and H. Basset, by the action of iodine on a neutral soln. of potassium chlorate; $2KClO_3+I_2+H_2O=KH(IO_3)_2+KCl+HOCl$; on an acidulated soln. of potassium chlorate: $5KClO_3+2I_2+3H_2O=2KCl+3HCl+3KH(IO_3)_2$; on evaporation there is a further reaction: $KIO_3.HIO_3+12HCl=KCl+ICl+ICl.HCl+4Cl_2+6H_2O$.

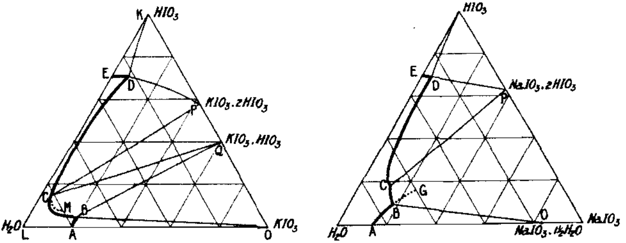
H. Klinger made the di-iodate by mixing 20 grms. of potassium chlorate, 21 grms. of iodine, and 100 c.c. of water in a half-litre tubulated retort with a thermometer fitted in the tubulure, and the neck directed upwards. The mixture is heated by a small flame. The liquid becomes yellow, and violet vapours condense in the neck of the retort. The materials begin to react at about 85°, and the reaction is complete at about 95°. Only a little chlorine is evolved when the liquid is heated up to its b.p. When the colourless liquid is cooled, crystals of the di-iodate separate, and these can be purified by recrystallization from hot water. The yield is over 70 per cent. Some barium di-iodate can be recovered by adding barium chloride to the mother-liquid.

J. C. G. de Marignac showed that the crystals are trimorphous, for they exist in three different forms: (i) Thick plates belonging to the rhombic system—Fig. 16; (ii) twinned pyramids belong to the monoclinic system—Fig. 17; and (iii) thick plates also belonging to the monoclinic system—Fig. 18. Aq. soln. redden litmus,

and have an acid taste. The crystals lose 2·3 per cent. of water at 150°, and at a higher temp. decompose into potassium iodide and oxygen; 100 grms. of water, at 15°, dissolve 1·33 grms. of the salt; and at 17°, 5·4 grms.[57] Alcohol dissolves virtually none. The salt can be crystallized from water at 30°. The heat of soln. is 11·8 Cals., and the heat of formation from solid iodate and iodic acid, 3·1 Cals.[58] The salt is decomposed by mineral acids, and by potassium iodide: $6KH(IO_3)_2+5KI=11KIO_3+3I_2+3H_2O$, G. S. Sérullas,[59] C. F. Rammelsberg, E. Filhol, and H. L. Wheeler prepared rhombic crystals of a double compound with potassium chloride, $KCl.KIO_3.HIO_3$.

N. A. E. Millon and A. Ditte made **potassium tri-iodate,** $KIO_3.2HIO_3$, by treating a mol. of potassium hydroxide with three mols. of iodic acid, and by the action of an excess of iodic acid on a soln. of the normal salt; and G. S. Sérullas made this salt by treating the normal iodate, or the di-iodate with mineral acids. The crystals form rhomboidal prisms belonging to the triclinic system, and acquire a reddish tinge after standing some time. When heated between 150° and 200°, they lose 3·25 per cent. of water; and on further heating, the crystals melt, and then decompose, forming potassium iodide, iodine, and oxygen. At 15°, 100 grms. of water dissolve 4·0 grms. of the salt. The aq. soln. deposits crystals of $KIO_3.HIO_3$. A soln. with a mol. of the salt in 32 litres has an electrical conductivity[60] 578; and in 1024 litres, 789.

The composition of all possible mixtures of the three components, KIO_3, HIO_3, and H_2O, can be represented by a point on the equilateral triangle, Fig. 19. The



FIGS. 19 and 20.—Equilibrium Diagrams of the Ternary Systems: $KIO_3-HIO_3-H_2O$ and $NaIO_3-HIO_3-H_2O$ at 30°.

curves *AB, BC, CD, DE,* and *CM* represent systems in which the composition of the soln. are indicated. The points, *K, L,* and *O,* represent respectively 100 per cent. of HIO_3, 100 per cent. H_2O, and 100 per cent. KIO_3. The points *P* represent the composition of the binary salt $KIO_3.2HIO_3$; and *Q* the composition of the binary salt $KIO_3.HIO_3$. The curves *AB, BC, CD,* and *DE,* Fig. 19, represent the composition of soln. which are in equilibrium respectively with the solid phases: KIO_3, $KIO_3.HIO_3$, $KIO_3.2HIO_3$, and HIO_3. The point *A* represents the solubility of potassium iodate, and *E* the solubility of iodic acid in water at 30°. The curves intersect at the points *B, C, D;* and these points represent the composition of soln. which are in equilibrium with two solid phases. Thus, at *B,* the soln. is in equilibrium with the salts KIO_3 and $KIO_3.HIO_3$; at *C,* with the salts $KIO_3.HIO_3$ and $KIO_3.2HIO_3$; and at *D,* with the salt $KIO_3.2HIO_3$ and solid iodic acid, HIO_3. The curve *ABCDE* cuts the triangle into two parts: (1) The region *ABCDEL* represents a complex of the three components which at 30° form an unsaturated soln.; (2) The region *ABCDEKO* represents a complex which at 30° splits into a soln. and one or two solid phases—the lines *BO, BQ, CQ, CP, DP,* and *DK* have been drawn in order to show how the splitting occurs. Any point in the sectors

ABO, *CBQ*, *CDP*, and *EDK* represents a soln. which separates at 30° into a soln. whose composition is represented by a point on the curve *AB*, *BC*, *CD*, or *DE* and into one of the solid phases KIO_3 : $KIO_3.HIO_3$; $KIO_3.2HIO_3$; or HIO_3. A point in the triangle *BOQ*, *CPQ*, or *DPK* represents a soln. which at 30° separates into the soln. *B*, *C*, or *D*, and two salts respectively KIO_3 and $KIO_3.HIO_3$; $KIO_3.2HIO_3$; or $KIO_3.2HIO_3$ and HIO_3. In some cases, labile or metastable systems may be formed ; for example, a soln. of the composition represented by the point in the triangle *CPQ*, Fig. 19, instead of separating into the two solid phases $KIO_3.HIO_3$ and $KIO_3.2HIO_3$ and a soln. of the composition *C*, separates into the solid phase $KIO_3.2HIO_3$ and a soln. represented by a point on the curve *CM*. The di-iodate can be crystallized from pure water, at 30°, but with the tri-iodate, unstable di-iodate may separate out.

It has been claimed that **sodium di-iodate,** $NaIO_3.HIO_3$, can be made by adding sodium iodate, $NaIO_3$, to an aq. soln. of iodine chloride, and precipitating the acid salt with alcohol ; but G. S. Sérullas[61] stated that negative results are obtained, for the ordinary iodate is precipitated—C. F. Rammelsberg, A. Ditte, and N. A. E. Millon likewise failed. N. A. E. Millon said that he was unable to obtain, by analysis, *aucun résultat assez pour être enregistré*. F. Penny claimed to have made the salt $NaIO_3.HIO_3$ by the action of nitric acid upon sodium iodate ; and $NaIO_3.2HIO_3$, by using a considerable excess of nitric acid—but F. Penny gives no analysis of his products. C. W. Blomstrand prepared **sodium tri-iodate,** $NaIO_3.2HIO_3.\frac{1}{2}H_2O$, but not the di-iodate. It is probable that C. W. Blomstrand's tri-iodate is anhydrous and not hydrated as he supposed. It is obtained by spontaneous crystallization from a soln. containing a mol. of the sodium salt with about four mol. of iodic acid. C. W. Blomstrand says :

A small portion of the soln. dries to a transparent gum-like mass, but a large quantity of soln., after some days, begins to deposit on the basin near the surface a ring of a substance resembling chalk, and which consists of very fine particles, and radiating masses then extend deeper into the soln. From time to time, the solid is removed from the liquid by means of a spoon, and as much of the mother liquor as possible removed by press. The residual solid is a dry fine crystalline powder.

According to M. Weibull, the crystals probably belong to the cubic system.

P. A. Meerburg's equilibrium curve for the ternary system, $NaIO_3-HIO_3-H_2O$, is shown in Fig. 20, and the diagram is interpreted like that for the ternary system, $KIO_3-HIO_3-H_2O$. The solid phases are $NaIO_3.1\frac{1}{2}H_2O$; $NaIO_3.2HIO_3$, and the pyro- or anhydro-salt, $Na_2O.2I_2O_5$, *i.e.* $2NaIO_3.I_2O_5$. The curve *AB* represents the composition of soln. in equilibrium with $NaIO_3.1\frac{1}{2}H_2O$; *BC*, of soln. in equilibrium with $Na_2O.2I_2O_5$; *CD*, $NaIO_3.2HIO_3$; and *DE*, the composition of soln. in equilibrium with solid HIO_3. The composition of the **sodium anhydro-iodate,** $2NaIO_3.I_2O_5$, or $Na_2I_4O_{11}$, is not shown in Fig. 20, but it is indicated in the incomplete diagram, Fig. 21, representing the ternary system, $I_2O_5-H_2O-Na_2O$. Here, the point *P* represents the composition of the solid phase, $I_2O_5.H_2O$, or HIO_3 ; *Q*, $3I_2O_5.Na_2O.2H_2O$, or $NaIO_3.2HIO_3$; *R*, $Na_2O.2I_2O_5$, or $2NaIO_3.I_2O_5$; *S*, $Na_2O.I_2O_5.3H_2O$, or $NaIO_3.1\frac{1}{2}H_2O$; and *T*, $Na_2O.3H_2O$, or $NaOH.H_2O$. The curve *ABCDFG* is given diagrammatically ; the dotted line has not been explored. The line *AB* represents the composition of a soln. in equilibrium with the solid phase I_2O_5, H_2O, or HIO_3 ; *BC*, with $3I_2O_5.Na_2O.2H_2O$, or $NaIO_3.2HIO_3$; *CD*, with $2I_2O_5.Na_2O$, or $2NaIO_3.I_2O_5$; *DEF*, with $I_2O_5.Na_2O.3H_2O$, or $NaIO_3.1\frac{1}{2}H_2O$; and *FG*, $Na_2O.3H_2O$, or $NaOH.H_2O$. The points *A* and *G* represent the solubility at 30° of pure iodic acid and $NaOH.H_2O$ respectively ; the point *B*, *C*, *D*, and *F* are quadruple points representing soln. in equilibrium with two solid phases.

H. L. Wheeler[62] prepared **rubidium di-iodate,** $RbIO_3.HIO_3$, by mixing warm soln. containing one mol. of iodine pentoxide and two of rubidium chloride : $RbCl+2HIO_3=RbIO_3.HIO_3+HCl$. The acid iodate separates as a sparingly soluble crystalline powder on cooling. The acid iodate dissolves in hot water, and

the normal iodate separates on cooling. **Rubidium tri-iodate,** $RbIO_3.2HIO_3$, separates as a sparingly soluble crystalline powder during the cooling of a hot soln. of 5 grms. of rubidium iodate and 13 grms. of iodine pentoxide in 100 c.c. of water, boiled down to half its volume. As with the di-iodate, the tri-iodate dissolves in hot water and the soln. deposits the normal iodate on cooling. When a moderately dil. soln. of two mol. of cæsium chloride is mixed with a mol. of iodine pentoxide dissolved in a little water—dissolving any precipitate which may be formed by the addition of more water and heat—a sandy powder of **cæsium anhydro-iodate,** $2CsIO_3.I_2O_5$, is formed. It can be recrystallized from dil. soln. of iodic acid or even water alone without decomposition. H. L. Wheeler also obtained **cæsium acid anhydro-iodate,** $2CsIO_3.I_2O_5.2HIO_3$, by mixing 5 grms. of anhydro-iodate, $2CsIO_3.I_2O_5$, to a boiling soln. of 25 grms. of iodine pentoxide in a little water. When water is added, the compound is precipitated.

A series of complex salts—**halogenato-iodates**—have been formed by the union of the iodates or iodic acid with the alkali halides. For example, G. S. Sérullas[63] obtained rhombic crystals of the compound $KCl.KIO_3.HIO_3$, or $KCl.KH(IO_3)$, by incompletely saturating a soln. of iodine trichloride with potassium hydroxide, or carbonate, or by warming normal potassium iodate with dil. hydrochloric acid (1 : 10), allowing the respective soln. to evaporate spontaneously. The crystals are stable in air, and 100 grms. of water dissolve 5·26 grms. of the salt. Cold alcohol extracts potassium chloride from the crystals. The salt does not decompose at 100°; and it loses water at 260°. J. C. G. de Marignac found the axial ratios of the crystals to be $a : b : c = 1·1483 : 1 : 0·8847$; while those of $KIO_3.HIO_3$ are $1·1470 : 1 : (3 \times 0·8725)$. Other related complexes are E. Filhol's $KCl(HIO_3)_2$ and $KCl(KIO_3)_2$;[64] C. F. Rammelsberg's $(NaCl)_3(NaIO_3)_2.9H_2O$; $(NaCl)_2(NaIO_3)12H_2O$; $NaBr.NaIO_3.6H_2O$, and the same salt with $9H_2O$; F. Penny's $(NaI)_3(NaIO_3)_2.19H_2O$, which, according to C. F. Rammelsberg and J. C. G. de Marignac, contains $20H_2O$ not $19H_2O$; H. L. Wheeler's $RbCl.HIO_3$; $CsCl.HIO_3$; and $(RbCl)_3HIO_3$; and A. Michael and W. T. Conn's HI_7O_3, which is considered to be $(I_2)_3.HIO_3$, and is formed by the action of iodine on perchloric acid, $HClO_4$.

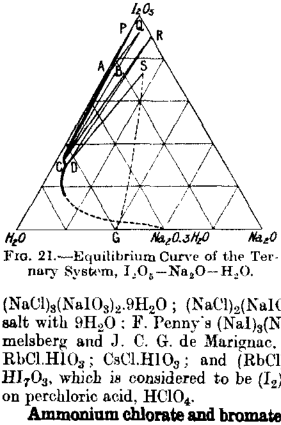


FIG. 21.—Equilibrium Curve of the Ternary System, $I_2O_5-Na_2O-H_2O$.

Ammonium chlorate and bromate, NH_4ClO_3 and NH_4BrO_3.—J. L. Gay Lussac[65] prepared ammonium chlorate by the action of an aq. soln. of chloric acid on aqua ammonia or ammonium carbonate; and R. Chenevix and A. Wächter by treating barium, strontium, or calcium chlorate with ammonium carbonate. C. Löwig prepared ammonium bromate by analogous methods. J. J. Berzelius also made ammonium chlorate by the action of ammonium fluosilicate, $(NH_4)_2SiF_6$, on potassium chlorate and decanted the soln. from the sparingly soluble potassium fluosilicate, K_2SiF_6, was precipitated; while J. Wonfor used ammonium hydrogen tartrate and potassium chlorate, and decanted the soln. from the sparingly soluble potassium tartrate. H. Kämmerer made ammonium bromate by heating iodic acid or potassium iodate with an excess of conc. ammonia for 8 hrs. at 110°—potassium iodide and ammonium bromate were produced. According to C. F. Schönbein, a small amount of ammonium chlorate is formed in the action of chlorine on aq. ammonia, and the bromate, by the action of bromine on ammonia. H. Erdmann thus describes the process:

Slowly run 75 c.c. of bromine from a dropping-funnel, with the stem drawn to a fine point. into 220 c.c. of conc. 30 per cent. ammonia contained in a flask surrounded by ice-water,

The reaction is $8NH_3+3Br_2=6NH_4Br+N_2$. The liquid should remain strongly ammoniacal during the addition of the bromine, and it should be continually shaken. If the bromine is run in too rapidly, or if the liquid becomes acid, the explosive nitrogen bromide may be formed. Heat the liquid until all the free ammonia is driven off, and evaporate the soln. to enable the ammonium bromate to crystallize. Dry the ammonium salt by warming the dish over a flame. The yield is 220 grms. of ammonium bromate.

According to J. Grossmann, ammonium chlorate is made by the action of sodium chlorate on a soln. of ammonium chloride; when the liquor is conc. by evaporation in a steam-jacketed enamelled pan, crystals of sodium chloride separate out, and the hot filtered liquor, on cooling, gives a crop of crystals of ammonium chlorate. Ammonium chlorate is explosive, and the crystals may explode spontaneously in a short time or in a few months; and G. E. Davis[66] reported an explosion of the soln. while being conc. in steam-jacketed pans, with demolition of the buildings in which the operations were being conducted. The boiling aq. soln. decomposes into chlorine and nitrogen; and according to A. Wächter, the solid decomposes when heated to 102°; when projected on to a cold plate; and in contact with organic matter (E. Mitscherlich). The products of the decomposition are chlorine, nitrogen, water, hyponitrous acid, and a little oxygen and ammonium chloride. Similar remarks apply to the bromate. According to A. Ries,[67] the white needle-like crystals of ammonium chlorate are probably rhombohedral and isomorphous with potassium chlorate; the crystals of ammonium bromate are probably trigonal like potassium bromate and are not isomorphous with potassium bromate. The crystals of both the chlorate and bromate have a piquant taste; they are very soluble in water, and almost insoluble in aq. alcohol. The sp. vol. of a soln. of ammonium chlorate is 0·986330, and the volume of a soln. containing ½ an eq. of the salt is 1972·661 when the computed volume is 1976·290. J. H. Gladstone found the refraction eq. of 4·53 and 21·75 per cent. soln. of ammonium chlorate to be respectively 29·51 and 28·75 for the *F*-line, and 33·14 and 30·01 for the *H*-line.

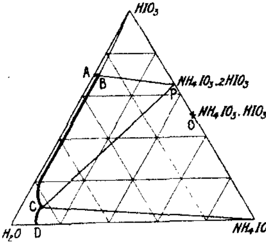


FIG. 22.—Equilibrium Diagram for Solutions in the Ternary System, $NH_4IO_3-HIO_3-H_2O$

Ammonium iodate, NH_4IO_3.—This salt is formed by H. Kämmerer[68] as a sparingly soluble white crystalline powder by the neutralisation of aq. iodic acid, or iodine trichloride with ammonia or ammonium carbonate; from iodine water and ammonia; from cold soln. of ammonium carbonate and barium iodate. A. Guyard, and F. D. Chattaway and K. J. P. Orton, also noticed that when nitrogen iodide is suspended in aqua ammonia and exposed to sunlight, ammonium iodide and iodate are formed.

According to A. S. Eakle[69] the crystals belong to the rhombic system, but A. Ries says that it is more probable that they belong to the monoclinic system—with a pseudo-cubic form and axial ratios $a:b:c=0·9951:1:1·4299$; $\beta=90°\ 0'$. F. W. Clarke[70] gives the sp. gr. at 12·5° as 3·3372, and at 21°, 3·3085 referred to water at 4°. According to C. F. Rammelsberg, the solubility in 100 grms. of water is 2·06 grms. at 15°, and 14·5 grms. in a boiling soln.; P. A. Meerburg found that water at 30° dissolved 4·20 per cent. of ammonium iodate, Fig. 22. H. Marbuch found that the crystals, but not the aq. soln., act on polarized light. The crystals decomposed with a hissing noise at 150°, into iodine, oxygen, nitrogen, and water vapour: $2NH_4IO_3=N_2+I_2+O_2+4H_2O$; and they detonate when projected on glowing charcoal; and conc. hydrochloric acid also converts them into ammonium tetrachloro-iodide, NH_4ICl_4. According to A. Ditte, white crystals of **hemihydrated**

ammonium-iodate, $2NH_4IO_3.H_2O$, separate from a boiling soln. of iodic acid, sat. with ammonia; the crystals are stable at 106°, but decompose explosively at 150°.

C. W. Blomstrand found that crystals of the normal iodate separate when eq. soln. of iodic acid and ammonium iodate are mixed together; while A. Ditte claimed that crystals of **ammonium di-iodate,** $NH_4IO_3.HIO_3$, are produced at 70°. P. A. Meerburg, in confirmation of C. W. Blomstrand, could find no sign of the alleged di-iodate at 30°, and his equilibrium diagram of ternary soln.: $NH_4IO_3-HIO_3-H_2O$, at 30°, is shown in Fig. 22. **Ammonium tri-iodate,** $NH_4IO_3.2HIO_3$, *i.e.* $(NH_4)H_2(IO_3)_3$, was, however, obtained by all three investigators in the form of triclinic crystals from soln. containing two eq. of iodic acid per eq. of ammonium iodate. In the diagram, *DC* represents the composition of the soln. in equilibrium with solid ammonium iodate, NH_4IO_3; *BC*, with the tri-iodate, $NH_4IO_3.2HIO_3$; *AB*, with iodic acid, HIO_3. The quadruple points *B* and *C* represent soln. in equilibrium with two solid phases. E. Riegler also prepared the tri-iodate by adding an aq. soln. containing the eq. of 3 grms. of NH_3 to a boiling aq. soln. of 100 grms. of iodic acid, HIO_3, and allowing the mixture to stand 24 hrs. The triclinic crystals have axial ratios $a:b:c=0.5693:1:?$, and $\alpha=81°\ 17'$; $\beta=115°\ 8'$; $\gamma=90°\ 49'$. E. Riegler proposes this complex salt for standardizing soln. in volumetric analysis.

Silver chlorate, $AgClO_3$.—R. Chenevix (1802)[71] obtained a silver chlorate by leading chlorine gas into water in which silver oxide was suspended, until oxygen began to be formed. J. S. Stas prepared the same salt in a similar manner, using either the oxide or the carbonate. Silver chloride and hypochlorite are first formed, and part of the latter is hydrolyzed to hypochlorous acid, which then reacts with another part of the silver hypochlorite to form silver chloride and chlorate. The clear liquid is decanted from the chloride and evaporated until the chlorate crystallizes out. L. N. Vauquelin made the salt by dissolving silver oxide in chloric acid; and W. S. Hendrixson by the action of chloric acid on finely divided silver: $6Ag+6HClO_3=AgCl+3H_2O+5AgClO_3$. Silver chlorate exists in two forms: (i) stable white opaque tetragonal prisms with the axial ratio $a:c=1:0.9325$, and sp. gr. according to H. G. F. Schröder,[72] 4·42 to 4·44; or, according to J. W. Retgers, 4·401 at 23°; (ii) Labile cubic crystals with a sp. gr. of 4·21 according to J. W. Retgers. Like potassium chlorate, silver chlorate does not change in dry or moist air. L. N. Vauquelin says that 100 parts of cold water dissolves about 9 grms. of the salt, while A. Wächter gives nearly twice this amount—namely, 20 grms. The salt dissolves readily in alcohol. M. Löb and W. Nernst give the eq. conductivity of a soln. containing 0·0008 and 0·025 mol. of $AgClO_3$ per litre as 1163 and 1045 respectively; the transport number of the anion in 0·02*N*-soln. is given as 0·505. According to A. Wächter (1843), silver chlorate melts at 230°, and develops oxygen at 270°, leaving a residue of silver chloride; with very rapid heating the salt may decompose explosively. G. Gore[73] obtained a black deposit—possibly silver peroxide—upon the anode during the electrolysis of soln. of silver chlorate. Dry chlorine, according to J. Krutwig, converts silver chlorate into silver chloride and chlorine dioxide; and in aq. soln., chlorine forms silver chloride, chloric acid, and some oxygen. With hydrochloric, nitric, and acetic acids, silver chloride and oxygen are formed. G. Bruni and G. Levi prepared **triammino-silver chlorate**, $AgClO_3.3NH_3$.

Silver bromate, $AgBrO_3$.—A. J. Balard[74] precipitated silver bromate, $AgBrO_3$, as a white powder by adding bromic acid or potassium bromate to a soln. of silver nitrate; the powder darkens in light. J. S. Stas says that the precipitate is contaminated with an appreciable quantity of silver nitrate, and he recommends precipitating the salt by adding a neutral one per cent. soln. of silver sulphate to a 3 per cent. soln. of potassium bromate—if the silver sulphate is not quite neutral, the precipitate will be contaminated with silver bromide, and the supernatant liquor will appear more or less milky, and be coloured violet or purple in light. J. S. Stas also made silver bromate, by treating a 5 per cent. soln. of silver dithionate, $Ag_2S_2O_6$, with a 5 per cent. soln. of potassium bromate, all at 0°; a white precipitate is formed which is thoroughly washed by decantation with cold water, and recrystallized from

its soln. in boiling water. The salt, dried at 150°, in vacuo, contains a trace of water which can be expelled only by fusion. The crystals of silver bromate belong to the tetragonal system[75] with the axial ratio $a:c=1:0.943$, and sp. gr. according to F. W. Clarke of 5·1983 to 5·2153. The solubility of silver bromate at 20° is 1·586 grms. per litre (W. Böttger);[76] at 24·5°, 1·911 (A. A. Noyes); and at 25°, 1·68 (A. Longi). According to A. Longi, a soln. in 5 per. cent. ammonia (sp. gr. 0·998) contains 3·51 grms. of $AgBrO_3$ per 100 c.c. of soln., or 3·554 grms. of salt per 100 grms. of soln.; and 100 c.c. of a 10 per cent. ammonia soln. (sp. gr. 0·96) contains 44·36 grms. of salt per 100 c.c. of soln., or 46·25 grms. per 100 grms. of soln.; and a soln. in 35 per cent. nitric acid (sp. gr. 1·21) contains 0·381 grm. of salt per 100 c.c., or 0·312 grm per 100 grms. of soln. A. A. Noyes showed that the solubility is depressed in presence of silver nitrate or potassium bromate. According to C. F. Rammelsberg,[77] a sat. soln. of silver bromate in aq. ammonia deposits, on conc., crystals of diamminosilver bromate, $AgBrO_3.2NH_3$, a salt which readily decomposes into nitrogen, water, and silver bromide; it also decomposes with a hissing noise when warmed. According to J. S. Stas, highly purified silver bromate is stable in light in air free from organic matter, and its soln. can be boiled, without change, in direct sunlight. It decomposes when heated, forming oxygen and silver bromide. If rapidly heated the salt may detonate. G. Bruni and G. Levi prepared **triammino-silver bromate**, $AgBrO_3.3NH_3$.

Silver iodate, $AgIO_3$.—A mixture of silver iodate and iodide was made by C. Weltzien (1854)[78] and A. Naquet, by the action of iodine in aq. or alcoholic soln on an excess of silver oxide or nitrate; by W. S. Hendrixson by the action of iodic acid on finely divided silver; by C. W. B. Normand and A. C. Cumming by the prolonged action of iodine on silver cyanate; by W. Pawloff and S. Schein by the action of iodine on silver nitrate; by J. L. Gay Lussac (1815) and A. Ladenburg (1865), by treating a soln. of silver nitrate with iodic acid, or, according to C. F. Rammelsberg, sodium iodate. A. Ditte obtained good crystals by cooling dil. hot soln. of silver nitrate and potassium iodate in the presence of much nitric acid. The difficulty of washing silver nitrate from these precipitates led J. S. Stas to treat silver sulphate with iodic acid; or silver dithionate, $Ag_2S_2O_6$, with potassium iodate. The precipitate is washed with cold water, then with hot water, by means of suction. The precipitate is sufficiently finely divided for adequate washing when made in dil. soln.—say 2½ per cent. A. E. Hill and J. P. Simmons purified silver iodate by dissolving the washed precipitate in aqua ammonia, and reprecipitating by the addition of nitric acid, and again washing the product. The precipitate is at first amorphous, but it slowly changes into the crystalline condition by agitation with nitric acid. The product is dried at 130°–150° in a current of dry air free from organic matter. N. A. E. Millon, however, has shown that the salt retains traces of water very tenaciously at 200°.

Rhombic crystals separate from aq. ammonia in small prisms free from ammonia. The axial ratios are $a:b:c=0.8832:1:1.3072$. According to F. W. Clarke,[79] the sp. gr. of precipitated silver iodate at 16·5° is 5·4023; and of the salt crystallized from ammonia, at 16·5°, is 5·6475. It melts when heated with but slight decomposition, and at a higher temp. it decomposes into oxygen and silver iodide. According to J. S. Stas, it does not blacken in light if organic matter be excluded. Silver iodate is sparingly soluble in water, 100 c.c. of water at 18° dissolve 0·00014 mol. (F. Kohlrausch),[80] at 19·95°, 0·000154 mol. (W. Böttger); and at 25°, 0·000189 mol. (A. A. Noyes and D. A. Kohr). A. Longi found that 100 c.c. of 0·5 per cent. ammonia (sp. gr. 0·998) dissolve 1·134 grms. of silver iodate; 10 per cent. ammonia (sp. gr. 0·96), 42 grms.; and 35 per cent. nitric acid, 0·116 grm. According to A. E. Hill and J. P. Simmons, the solubility in nitric acid at 25° in grams and in equivalents per litre, is:

HNO_3	*N*- .	0	0·125	0·250	0·500	1·00	2·00	4·00	8·00
	Per cent.	0	0·788	1·564	3·096	6·128	11·757	22·277	40·425
$AgIO_3$	Grms. .	0·0503	0·0864	0·1074	0·1413	0·2067	0·3319	0·6935	1·587
	Eq. .	0·178	0·304	0·379	0·499	0·731	1·174	2·469	5·608

The amorphous variety is more soluble than the crystalline form. The salt is not decomposed by boiling nitric acid :[81] conc. sulphuric acid at 300° does not yield oxygen or iodine, but if organic matter be present the salt decomposes at 170°. Alkali lye decomposes silver iodate rapidly in the cold. Chlorine acts only on the heated salt, forming iodine trichloride. Hydrochloric acid acts: $AgIO_3+6HCl=AgCl+ICl_3+3H_2O+Cl_2$; iodine yields iodic acid and silver iodide ; boiling soln. of potassium iodide give silver iodide and potassium iodate ; conc. soln. of potassium iodide, in the presence of hydrochloric acid, furnish iodine, silver iodide, and potassium chloride: $AgIO_3+6KI+6HCl=AgI+6KCl+3I_2+3H_2O$. Gold is not attacked by iodic acid ; but a soln. of auric chloride, $AuCl_3$, with iodic acid or potassium iodate, gives a yellow precipitate of sparingly soluble **gold iodate.** The corresponding chlorate and bromate have not been made.

Cupric chlorate, $Cu(ClO_3)_2$.– L. N. Vauquelin (1815)[82] and J. Traube (1895) obtained bluish-green soln. by the dissolution of cupric oxide or carbonate in chloric acid ; and by evaporating the analogous soln. obtained by the action of cupric sulphate on barium chlorate, *in vacuo*, over sulphuric acid, dark green crystals of what are said to be hexahydrated cupric chlorate, $Cu(ClO_3)_2.6H_2O$, were obtained by A. Wächter, in 1843. The crystals are unstable in air ; they melt at 65°, freeze again at 20°. At 100°, the salt gives off gas bubbles, and this the more vigorously as the temp. rises to 110° or 120°. The gases are chlorine dioxide, chlorine, and oxygen. According to J. Traube, aq. soln. at 15° have, with

Per cent. $Cu(ClO_3)_2$.	2·106	4·778	6·945	10·016	14·387
Specific gravity . .	1·01620	1·03857	1·05714	1·08444	1·12531
Mol. solution volume .	47·0	47·4	48·5	49·5	51·0

The lowering of the f.p. of water by the soln. of 2·106 per cent. $Cu(ClO_3)_2$ is 0·485°, so that the molecular depression is 53·1. The crystals are soluble in alcohol. It is probable that the alleged hexahydrated chlorate is a tetrahydrated chlorate, for, according to A. Meusser, the solubility curve shows no signs of the hexahydrate, but only **tetrahydrated cupric chlorate,** $Cu(ClO_3)_2.4H_2O$. The solubility represented by the number of grams of cupric chlorate, $Cu(ClO_3)_2$, in 100 grms. of soln. at different temp., in presence of the solid phase $Cu(ClO_3)_2.4H_2O$, is

	−31°	−21°	0·8°	18°	45°	59·6°	71°
Solubility	54·59	57·12	58·51	62·17	66·17	69·42	76·90

Ice is the solid phase below −12°, when the solubility is 30·5 per cent., and at −25°, 39·1 per cent., the solid melts at 73°. Possibly at this temp. a lower hydrate is formed.

A **basic copper chlorate** is formed when soln. of potassium chlorate acidified with sulphuric acid are electrolyzed with an alternating current between copper electrodes (L. Rossi) ;[83] when the hydrate is heated above 100° (A. Wächter) ; when a soln. of copper chlorate be mixed with pieces of marble or urea, and heated in a sealed tube to 130° (L. Bourgeois) ; when the hydroxides of the alkalies or alkaline earths act on cupric chlorate soln., or copper hydroxide acts on soln. of potassium chlorate (A. Brochet) ; when hydrated cupric oxide or cupric hydroxide acts on cupric chlorate soln. (P. Sabatier) ; or when potassium chlorate acts on cupric acetate soln. (A. Casselmann), basic cupric chlorate is obtained. The basic chlorate forms bluish-green monoclinic prisms ; of sp. gr. 3·55 ; and composition $4CuO.Cl_2O_5.3H_2O$, that is, $Cu(ClO_3)_2.3Cu(OH)_2$, which A. Werner considers to be *hexahydroxyl cupric chlorate* :

$$\left[Cu\left(\begin{matrix}HO\\HO\end{matrix}Cu\right)_3\right](ClO_3)_2$$

This basic chlorate is very sparingly soluble in water, very soluble in dil. acids, and the soln. in dil. nitric acid gives no precipitate with silver nitrate ; the soln. in hydrochloric acid smells of chlorine. Its solubility in a conc. soln. of cupric

chlorate is proportional to the temp. and conc. of the soln. The basic chlorates have not been studied from the point of view of the phase rule.

F. Ephraim and A. Jahnsen prepared a number of ammino-compounds or ammoniates of the metal chlorates bromates, and iodates (i) by passing ammonia into a conc. aq. soln. of the metal; (ii) by adding ethyl alcohol sat. with ammonia to the metal salt; or (iii) by heating the salt at a suitable temp. in a stream of ammonia. **Copper tetrammino-chlorate,** $Cu(ClO_3)_2.4NH_3$, forms deep-blue needles with a sp. gr. 1·81, mol. vol. 164·9, and a dissociation press. of 36 mm. at 97°; 55 mm. at 116°; and 715 mm. at 158°. **Copper hexammino-chlorate,** $Cu(ClO_3)_2.6NH_3$, forms deep-blue crystals with a dissociation press. of 201 mm. at −15°; 286 mm. at −1°; 380 mm. at 10°; 491 mm. at 20°; 628 mm. at 31°—with some evidence of the formation of a solid soln. Many of these ammino-compounds explode when heated or by percussion. The explosion in an open tube is believed to occur at the temp. at which the dissociation press. reaches one atm., because "below the dissociation temp., the splitting off of ammonia molecules is an endothermal process, but above the dissociation temp. an exothermal process." Copper tetra-ammino-chlorate explodes in an open and closed tube respectively at 208° and 289°; and the hexa-ammino-chlorate at 201° and 240°. The heats of formation, Q, calculated by A. Jahnsen from $\log p = -Q/4{\cdot}571T + 1{\cdot}75T + 3{\cdot}8$ are 15·6 Cals. for the tetrammino-salt, and 9·8 Cals. for the hexammino-salt.

Copper bromate, $Cu(BrO_3)_2$.—This salt is obtained in a similar manner to the chlorate, forming deep blue octahedral crystals, with sp. gr. 2·583. C. F. Rammelsberg's analyses[84] make the composition $Cu(BrO_3)_2.5H_2O$, H. Topsöe's analyses, $Cu(BrO_3)_2.6H_2O$. The crystals do not effloresce in air, but over conc. sulphuric acid they form a green powder. The crystals lose most of their water at 180°, and the last trace with some bromine is lost at 200°. As with the chlorate, basic bromate is said to be formed when the hydrated bromate is heated; and when the normal salt is incompletely precipitated by ammonia. C. F. Rammelsberg gives for the composition of the basic bromate $6CuO.Br_2O_6.10H_2O$; that is, $Cu(BrO_3)_2.5Cu(OH)_2.5H_2O$. C. F. Rammelsberg, and A. Jahnsen prepared **cupric tetrammino-bromate,** $Cu(BrO_3)_2.4NH_3$. At room temp. the salt takes up no more ammonia. Its sp. gr. is 2·31; mol. vol. 167·7; its heat of formation 14·9 Cals.; it detonates in an open capillary tube at 140°, and in a closed tube at 148°–150°; and it also detonates when struck with a hammer.

Copper iodate, $Cu(IO_3)_2$.—Copper iodate is not precipitated when iodic acid is added to a soln. of cupric nitrate, because the nitric acid liberated by the double decomposition is soluble therein. C. F. Rammelsberg in 1838, and N. A. E. Millon[85] in 1845, made a soln. of copper iodate. A. Pleischl (1825) noted a similar result is obtained by dissolving copper hydroxide or carbonate in iodic acid. A greenish-white precipitate is formed when a mixed soln. of iodic acid or sodium iodate and copper nitrate, acetate, or sulphate is allowed to stand for a few hours, or, if the soln. be acidified with nitric acid and warmed to 40° or 50° (A. Ditte); A. Granger, and A. de Schulten gradually dropped a soln. of 20 grms. of potassium iodate in two litres of water into a soln. of 30 grms. of cupric nitrate in 100 c.c. of water and 50 c.c. of nitric acid (sp. gr. 1·33) heated on a water-bath. After standing 6 days, 11 grms. of crystals of the salt can be collected. According to J. F. Spencer, a pale-blue precipitate is formed when potassium iodate is added to a soln. of cupric nitrate; the precipitate dissolves when the soln. is shaken, but if an excess of the potassium iodate be added, a pale-blue crystalline precipitate is formed. The precipitate can be washed with water and dried in air. The pale-blue triclinic crystals have a sp. gr. 4·876 at 15°, and their composition corresponds with the **monohydrated cupric iodate,** $Cu(IO_3)_2.H_2O$. The axial ratios are $a:b:c = 1{\cdot}2898:1:1{\cdot}5188$; $\alpha = 82°\ 38'$; $\beta = 95°\ 0'$; $\gamma = 91°\ 6'$; the sp. gr. 4·876. This iodate loses water between 240° and 250°, the water of crystallization is taken up again very slowly when the dehydrated salt is placed in water; when cupric iodate is heated to a still higher temp. it gives off iodine and oxygen, and leaves a residue of cupric

oxide. 100 grms. of water dissolve 0·33 grm. of this hydrate at 15°; and 0·65 at 100°. J. F. Spencer found 0·0033 mol. dissolved at 25°, and he could detect no evidence of the formation of complex salts in the presence of potassium iodate or cupric sulphate, because the depression of the solubility in the presence of these salts is normal. Cupric iodate is soluble in aq. ammonia and dil. sulphuric acid; the soln. in hydrochloric acid gradually decomposes with the evolution of chlorine, etc. N. A. E. Millon reported a hydrate, $3Cu(IO_3)_2.2H_2O$, but it is probably a mixture. Anhydrous cupric iodate is formed when a sat. soln. of the monohydrated salt in conc. nitric acid is heated between 70° and 80° for some time. Pale-green monoclinic plates of sp. gr. 5·241 at 15° are formed; the crystals, in contact with water, form the monohydrated salt on standing a few days. A. Jahnsen prepared the anhydrous iodate by drying the monohydrate at 240°, the product is pale brown, but no free iodine can be detected in the product. It has a sp. gr. 48·3, and mol. vol. 85·6. **Basic copper iodate** corresponding with $2CuO.I_2O_5.\frac{2}{3}H_2O$ has been reported by N. A. E. Millon (1845) and A. Ditte (1890); and $2CuO.I_2O_5.H_2O$, or $Cu(IO_3)_2.Cu(OH)_2$, or $Cu(IO_3)OH$ by A. Granger and A. de Schulten (1904). The latter is produced by the action of potassium iodate on a warm faintly acid dil. soln. of copper sulphate. The dark-green rhombic crystals have a sp. gr. 4·878, and axial ratios $a:b:c=0·7124:1:1·7073$. Many basic salts may or may not prove to be chemical individuals when investigated in the light of the phase rule. C. F. Rammelsberg, and F. Ephraim and A. Jahnsen prepared **dihydrated copper tetrammino-iodate,** $Cu(IO_3)_2.2H_2O.4NH_3$, in blue prisms by the action of ammonia on an ammoniacal soln. of copper nitrate. The compound $Cu(IO_3).8NH_3.4H_2O$, reported by A. Ditte, is probably the tetrammino-salt. A. Ditte also made this salt by the action of ammonia on anhydrous cupric iodate. When this salt is dehydrated at 160° in a current of ammonia, it forms **copper tetrammino-iodate,** $Cu(IO_3)_2.4NH_3$; and when the latter compound is sat. with ammonia in the cold, it furnishes **copper pentammino-iodate,** $Cu(IO_3)_2.5NH_3$, of sp. gr. 2·72, and mol. vol. 183·2. The mol. vol. of each NH_3 in the complex is 19·5. The latter compound has a dissociation press. of 141 mm. at 50·5°; 260 mm. at 65°; 440 mm. at 70°; 640 mm. at 82°; and 719 mm. at 84·5°. The heat of formation, according to A. Jahnsen, is 12·7 Cals. These ammino-iodates do not explode when heated in an open tube, but in a closed tube they explode between 210° and 219°.

The chlorates of the alkaline earths.—These chlorates include calcium chlorate, $Ca(ClO_3)_2$; strontium chlorate, $Sr(ClO_3)_2$; and barium chlorate, $Ba(ClO_3)_2$. The barium salt is perhaps the most useful of the series because of its use in preparing the acid and other salts by double decomposition. The chlorate and chloride of the alkaline earth are formed by passing chlorine into water in which the hydroxide or carbonate is suspended. As previously indicated, the conditions for a maximum yield have been discussed by G. Lunge. It is difficult to separate the chlorate and chloride by fractional crystallization, and hence R. Chenevix and L. N. Vauquelin [86] crystallized out as much of the less soluble chloride as was practicable, and removed the remainder by adding silver phosphate. C. C. Moore used native calcium borate at 60°–80° in place of the carbonate or hydroxide: $3(Ca_2B_4O_7.3H_2O)+6Cl_2+9H_2O=12H_3BO_3+5CaCl_2+Ca(ClO_3)_2$; and recovered the crystals of boric acid by cooling to 15°. The chlorate is also made by neutralizing an aq. soln. of chloric acid with the hydroxide or carbonate of the alkaline earth; the chloric acid being obtained by double decomposition with potassium or sodium chlorate and an acid or acid salt which will give a sparingly soluble alkali salt. Thus, A. Wächter [87] treated potassium chlorate with hydrofluosilicic acid whereby potassium fluosilicate, K_2SiF_6, is precipitated, and a soln. of chloric acid is formed; L. Thompson treated potassium chlorate with ammonium bitartrate to get a precipitate of potassium tartrate, $KH_5C_4O_6$, and a soln. of ammonium chlorate; M. Brandau mixed potassium chlorate with aluminium sulphate and sulphuric acid, and added alcohol to precipitate alum —$K_2SO_4.Al_2(SO_4)_3.24H_2O$; A. Duflos treated sodium chlorate with tartaric acid

whereby sodium tartrate, $NaH_5C_4O_6$, is precipitated; and R. Böttger treated sodium chlorate with oxalic acid, whereby sodium oxalate, $Na_2C_2O_4$, was precipitated. In each case, the decanted liquid was neutralized with the hydroxide or carbonate of the alkaline earth, and the clear liquor conc. until the required salt crystallized from the soln. The chlorates of the alkaline earths have been made by the electrolysis of soln. of the chlorides (*q.v.*).[88] J. L. Wheeler, and T. B. Munroe made barium chlorate by treating sodium chlorate with hydrofluosilicic acid: $2NaClO_3+H_2SiF_6 \rightarrow 2HClO_3+Na_2SiF_6$; after settling, the soln. of chloric acid was decanted, and the precipitate washed. The chloric acid was then neutralized with barium carbonate, and the barium chlorate crystallized from the soln. The yield is about 66 per cent. The chief loss is due to the difficulty in separating the chloric acid and sodium fluosilicate.

Calcium chlorate separates in deliquescent, monoclinic crystals of the **dihydrated calcium chlorate,** $Ca(ClO_3)_2.2H_2O$, when its soln. are evaporated over conc. sulphuric acid. According to A. Wächter,[89] strontium chlorate under similar conditions gives rhombic crystals of the anhydrous salt, $Sr(ClO_3)_2$, where the axial ratios are $a:b:c=0.9174:1:0.6003$ (H. Topsöe); A. Potilitzin obtained needle-like crystals of **trihydrated strontium chlorate,** $Sr(ClO_3)_2.3H_2O$, by cooling a 59 per cent. soln. to $-40°$, and rhombic prisms by cooling a 64 per cent. soln. to $-20°$ or $-25°$; if the latter soln. be rapidly cooled to $-95°$ to $-98°$, it forms a gelatinous mass. Other less definite hydrates of strontium have been reported. The soln. of the barium salt furnishes monoclinic prisms of the **monohydrated barium chlorate,** $Ba(ClO_3)_2.H_2O$, where the axial ratios are $a:b:c=1.1416:1:1.1981$; $\beta=93° 34'$ (A. S. Eakle). E. Mallard,[90] H. Traube, J. W. Retgers, and R. Rea studied the isomorphism of the nitrate and chlorates. According to H. Traube, barium nitrate and chlorate form regular tetrahedra containing at most 12·5 per cent. of barium chlorate, and monoclinic crystals with not over 9·1 per cent. of the nitrate. Rhombic crystals of strontium nitrate and chlorate were obtained with not over 7·2 per cent. of the chlorate.

According to M. Trautz and A. Anschütz, the crystals of barium monohydrated-chlorate begin to form in darkness more rapidly than in light; they exhibit triboluminescence—that is, they develop a transient luminescence by friction, trituration in a mortar, or by shaking the crystals in a bottle; and according to A. Wächter, crystallizing barium chlorate also shows crystallo-luminescence—*i.e.* crystallization is attended by flashes of luminescence. P. Bray could detect no fluorescence when the crystals of barium chlorate were exposed to the Röntgen or to the Becquerel rays. The crystals of the hydrated barium chlorate have a sp. gr. 2·988, according to C. H. D. Bödeker; [91] 3·179, according to H. G. F. Schröder; the latter also gives 3·152 for the crystals of strontium chlorate.

The heat of formation [92] of barium chlorate, $Ba(ClO_3)_2$, from its elements is 181·2 Cals.; the heat of soln. of the monohydrate in 600 mol. of water is 11·24 Cals. The sp. ht., according to L. Godin, is 0·157 between 17° and 47°. Dihydrated calcium chlorate melts [93] in its water of crystallization about 100°, and if heated slowly, all the water can be expelled. According to I. Guareschi, the dehydration temperature is 50°, and the dry salt regains its water rapidly when exposed to the air, and is very deliquescent. According to W. H. Sodeau, anhydrous calcium chlorate decomposes: $2Ca(ClO_3)_2=2CaCl_2+6O_2$, and also $2Ca(OCl_3)_2=2CaO+2Cl_2+5O_2$ —180 times more chlorate decomposes by the first than by the second reaction—from 0·6 to 2·0 per cent. of chlorine accompanies the oxygen, whether the decomposition proceeds slowly at 4 mm. or at 760 mm. press. When anhydrous strontium chlorate is heated, it begins to give off oxygen at about 120°; and then melts. According to A. Potilitzin, the first reaction in the decomposition of strontium chlorate is the formation of the perchlorate, chloride, and oxygen: $11Sr(ClO_3)_2=9SrCl_2+2Sr(ClO_4)_2+25O_2$. A. Wächter found that monohydrated barium chlorate loses its water at 120°, some oxygen is given off at 250°, and it melts at about 400°; and, as L. N. Vauquelin noticed, the residue contains both barium

oxide and barium chloride. A. Potilitzin says the decomposition begins at 300°, at 310° only about 0·2 per cent. is decomposed in 80 mm.; between 378° and 383°, the decomposition proceeds in accord with the equation: $2Ba(ClO_3)_2 = BaCl_2 + Ba(ClO_4)_2 + 2O_2$, at first with increasing and then with a decreasing velocity, but only about 11·1 per cent. is decomposed in 3 hrs. at this temp.; between 403° and 405°, the speed of this reaction is nearly doubled. The solubility of the monohydrated barium chlorate in water has been determined by P. Kremers,[94] etc. M. Trautz and A. Anschütz find that the solid phase from the eutectic or cryohydric temp., −2·749° ±0·004°, is $Ba(ClO_3)_2.H_2O$, and the percentage amount of salt, calculated as $Ba(ClO_3)$ in the soln. at different temp., is

	−2·75°	0°	10°	20°	40°	60°	80°	105°	146°
Per cent. $Ba(ClO_2)_2$.	15·28	16·90	21·23	25·26	33·16	40·05	45·90	52·62	78·0

According to A. Étard, the sat. soln. of barium chlorate has a solubility S at $\theta°$ between 0° and 100°, $S=19·0+0·382\theta$. F. Mylius and R. Funk state that 100 grms. of water dissolve 174 grms. of $Sr(ClO_3)_2$ at 18°; or 100 grms. of a sat. soln. at this temp. contains 63·6 grms. of strontium chlorate, and the sp. gr. of the soln. is 1·839. Similarly, 100 grms. of a sat. soln. of hydrated calcium chlorate at 18° contains 64 grms. of calcium chlorate, $Ca(ClO_3)_2$; and the sp. gr. of the soln. is 1·729. According to W. Eidmann, hydrated barium and calcium chlorate are soluble in acetone; and sparingly soluble in absolute alcohol—the former colours the alcohol flame green, the latter red. The sat. aq. soln. of barium chlorate, say M. Trautz and A. Anschütz, boils at 105° and 760 mm. when the soln. contains 52·67 per cent. of salt; P. Kremers gives 111° as the boiling temp. of a sat. soln. G. Tammann found that the vap. press. of water at 100° was lowered 8·7 mm. by the dissolution of 8·54 grms. of barium chlorate, and 103·2 mm. by 86·29 grms. J. H. Gladstone found the refraction eq. of a 23·75 per cent. soln. of barium chlorate to be 52·72 for the A-line, 53·36 for the D-line, and 54·95 for the H-line.

The bromates of the alkaline earths.—The alkaline earth bromates are obtained by processes analogous to those employed for the chlorates. C. Löwig [95] treated an aq. soln. of the hydroxide with an excess of bromine; A. J. Balard used bromine chloride; C. Löwig and J. S. Stas treated the chloride or acetate with potassium bromate: $2KBrO_3 + BaCl_2 = 2KCl + Ba(BrO_3)_2$; and C. Löwig and C. F. Rammelsberg neutralized bromic acid with the carbonate or hydroxide. The bromates of the alkaline earths can also be prepared by the electrolysis of soln. of the bromides. J. Sarghel showed that the yield with barium bromide is smaller than with calcium or magnesium bromide.

Calcium bromate is obtained by the concentration of the aq. soln. in monoclinic crystals [96] of the **monohydrated calcium bromate,** $Ca(BrO_3)_2.H_2O$; and likewise with monoclinic crystals of **monohydrated strontium bromate,** $Sr(BrO_3)_2.H_2O$, which are isomorphous with barium chlorate, $Ba(ClO_3)_2.H_2O$, and **monohydrated barium bromate,** $Ba(BrO_3)_2.H_2O$. J. C. G. de Marignac's values for the axial ratios of the calcium salt are $a:b:c=1·2045:1:1·0835$; $\beta=97° 53'$; J. Behr's values for the axial ratios of the crystals of the strontium salt are $a:b:c=1·1612:1:1·2356$; $\beta=92° 38'$; and for the barium salt, J. C. G. de Marignac found $a:b:c=1·1486:1:1·2130$; $\beta=93° 2'$. According to H. Topsöe, the sp. gr. of monohydrated calcium bromate is 3·329; of the strontium salt, 3·773; and of the barium salt, 3·820. J. Behr also gives for the strontium salt 3·778; and for the barium salt, 4·253. A. Eppler gives for the barium salt, 4·195, and F. W. Clarke and F. H. Storer; 4·0395 at 17°, and 3·9918 at 18°. The crystals of calcium, strontium, and barium bromates show triboluminescence.[97] The calcium salt loses its water at 180°, and the anhydrous salt decomposes when heated to a higher temp. into calcium bromide and oxygen; the crystals of the hydrated strontium bromate do not lose their water at ordinary temp. in vacuo over conc. sulphuric acid, but the water is completely expelled and the dehydrated salt loses its oxygen and forms strontium bromide at a higher temp. According to A. Potilitzin,[98] oxygen begins to be evolved at about

240° without the salt melting. As the temp. rises, the speed of decomposition increases to a maximum when about 10–12 per cent. of oxygen has been given off. The main reaction furnishes oxygen and strontium bromide: $Sr(BrO_3)_2 = SrBr_2 + 3O_2$; and a secondary reaction results in the formation of strontium oxide, bromine, and oxygen: $2Sr(BrO_3)_2 = 2SrO + 2Br_2 + 5O_2$. The higher the temp. of decomposition the less the proportion of bromate converted into oxide—*e.g.* at 252°, 5 per cent. of oxide is formed: and at 287°, 0·52 per cent. Hydrated barium bromate loses its water completely at 170°. The evolution of oxygen begins at about 260° or 265°, and the decomposition is vigorous at 300°–305°, and some bromine vapour comes off. There is no sign of the formation of a perbromate, although A. Potilitzin (1890) argued that because the speed of decomposition shows two distinct maxima, the decomposition must take place in two stages; in one, $BaO(BrO_3)_2$ is formed, and in the other, $Ba(BrO_3)_2$; but this is an ill-founded hypothesis.

According to C. F. Rammelsberg, cold water dissolves very nearly its own weight of hydrated calcium bromate; one-third its weight of the corresponding strontium salt; and about $\frac{1}{130}$th of its weight of the barium salt. According to M. Trautz and A. Anschütz, the cryohydric temp. with barium bromate, $Ba(BrO_3)_2.H_2O$, is $-0·034° \pm 0·004°$, and the solid phase from 0° to 100° is the monohydrate. The percentage solubility is then

	−0·034°	0°	10°	20°	40°	60°	80°	90·65°
Per cent. $Ba(BrO_3)_2$.	0·28	0·286	0·439	0·652	1·310	2·271	3·521	5·39

W. Eidmann says barium bromate is not soluble iu acetone. W. D. Harkins has measured the effect of various salts on the solubility of barium bromate.

The iodates of the alkaline earths.—According to E. Sonstadt, sea-water contains one part of calcium iodate, $Ca(IO_3)_2$, in 250,000 parts of water; and it occurs as the minerals: *lautarite*, $Ca(IO_3)_2$; and *dietzeite*, $7CaIO_3.8CaCrO_4$, in Chili saltpetre.[99] Lautarite and dietzeite, says F. W. Clarke, are remarkable as the first definitely known iodates to be found in the mineral kingdom, although A. A. Hayes reported sodium iodate as long ago as 1844. According to A. de Schulten, native lautarite can be imitated by heating 400 grms. of sodium nitrate until it commences to decompose, and mixing the molten mass with 125 grms. of monohydrated calcium iodate. On slowly cooling the molten soln. and washing away the nitrate with cold water, fine triclinic crystals of anhydrous calcium iodate, 2 to 3 mm. long, are obtained—sp. gr. 4·591 at 15°.

Three hydrates of calcium iodate have been reported, but one is probably a mixture of the other two. Rhombic crystals of **hexahydrated calcium iodate,** $Ca(IO_3)_2.6H_2O$, separate from a mixture of soln. of calcium iodate in hot dil. nitric acid (A. Ditte); from a mixture of soln. of calcium nitrate or chloride with iodic acid (N. A. E. Millon)[100] or potassium iodate (C. F. Rammelsberg); by mixing a conc. aq. soln. of calcium chloride with a dil. alcoholic soln. of iodic acid (A. Ditte); and by adding a cold filtered soln. of bleaching powder to an alcoholic soln. of iodine or potassium iodide until the iodine has all dissolved, and acids no longer produce a precipitate (W. Flight). The rhombic crystals of hexahydrated calcium iodate[101] have axial ratios $a:b:c = 0·4357:1:0·5229$ when crystallized from dil. nitric acid; and $a:b:c = 0·6465:1:0·2768$ when crystallized from soln. containing a little calcium chromate. The crystals show a positive double refraction.

According to A. Ditte, if an excess of a boiling soln. of calcium nitrate be mixed with a boiling soln. of an alkali iodate, crystals of *tetrahydrated calcium iodate,* $Ca(IO_3)_2.4H_2O$, separate on cooling, but in repeating this work, F. Mylius and R. Funk always obtained crystals of a variable composition, and they therefore infer that the alleged tetrahydrated iodate is really a mixture of the hexa- and the mono-hydrates. They find that if the hexahydrate be suspended in water, and heated to boiling, small polyhedral crystals are obtained which correspond with **monohydrated calcium iodate,** $Ca(IO_3)_2.H_2O$. N. A. E. Millon (1843)

also showed that the hexahydrate loses the eq. of five molecules of water when dried at 100°, and the remaining molecule at 190°.

Strontium iodate furnishes two hydrates: According to C. F. Rammelsberg, **monohydrated strontium iodate,** $Sr(IO_3)_2.H_2O$, is formed as a white crystalline powder when hot soln. of strontium chloride and sodium iodate are mixed together: and, according to A. Ditte, the same hydrate is formed by crystallization from cold nitric acid soln. C. F. Rammelsberg also claims that if soln. of strontium chloride and sodium iodate are mixed together in the cold, small crystals of **hexahydrated strontium iodate** are formed.

J. L. Gay Lussac [102] made **monohydrated barium iodate,** $Ba(IO_3)_2.H_2O$, by dissolving iodine in baryta-water; R. de Grosourdy employed iodine trichloride with baryta water or barium carbonate suspended in water. C. F. Rammelsberg made it by heating barium periodate, and also by treating sodium iodate with a conc. aq. soln. of barium chloride; A. Ditte similarly used a dil. boiling soln. of barium nitrate. N. A. E. Millon boiled baryta water with an excess of iodic acid and washed the precipitate with water—the boiling is necessary to prevent the contamination of the precipitate with barium hydroxide, and the use of other salts in place of barium hydroxide increases the risk of contaminating the precipitate. G. Kassner made the monohydrated iodate by treating potassium ferricyanide with potassium iodide and barium hydroxide in dilute potash lye: $12K_3FeCy_6+2KI+10KOH+Ba(OH)_2=Ba(IO_3)_2+12K_4FeCy_6+6H_2O$. Monohydrated barium iodate forms monoclinic crystals [103] with the axial ratios $a:b:c=1.151:1:1.265$; $\beta=92° 22'$.

The anhydrous iodates are made by dissolving the monohydrated iodate in fused sodium nitrate. Anhydrous calcium iodate, as indicated above, forms triclinic crystals [104] of sp. gr. 4·591 with axial ratios $a:b:c=0.6331:1:0.6462$; $\beta=106° 22'$. Anhydrous strontium iodate forms triclinic crystals of sp. gr. 5·045 at 15°. The axial ratios are $a:b:c=0.9697:1:0.5346$; $\alpha=92° 23'$; $\beta=95° 48'$; and $\gamma=93° 37'$. Anhydrous barium iodate forms monoclinic crystals of sp. gr. 4·998 at 15°—F. W. Clarke gives 5·1853 to 5·2855—and the axial ratios are $a:b:c=1.0833;1:1.2403$; $\beta=94° 6'$. Monohydrated barium iodate loses its water of crystallization at 130° according to N. A. E. Millon, between 180° and 200° according to A. Ditte, and on further calcination, it loses iodine and oxygen, forming barium periodate.

The solubility of calcium iodate in water has been determined by J. L. Gay Lussac, and by C. F. Rammelsberg. The solubility of monohydrated calcium iodate calculated as anhydrous $Ca(IO_3)_2$ in the sat. soln. of $Ca(IO_3)_2.H_2O$, is:

	21°	35°	40°	45°	50°	60°	80°	100°
Per cent. $Ca(IO_3)_2$.	0·37	0·48	0·52	0·54	0·59	0·65	0·70	0·94

and of hexahydrated calcium iodate, $Ca(IO_3)_2.6H_2O$:

	0°	10°	18°	30°	40°	50°	54°	60°
Per cent. $Ca(IO_3)_2$.	0·10	0·17	0·25	0·42	0·61	0·89	1·04	1·36

The two curves cross at about 32°, and this temp. therefore represents the transition point of the mono- and hexa-hydrated iodates. Calcium iodate is but very sparingly soluble in conc. sulphuric acid; and much more easily soluble in nitric acid than in water. Soln. in hydrochloric acid soon decompose. It is slightly soluble in conc. soln. of potassium iodide. Calcium iodate is precipitated when alcohol is added to the aq. soln. E. Sonstadt claims that a little calcium iodate is present in sea water. According to J. L. Gay Lussac,[105] 100 grms. of water at 15° dissolve 0·23 grms. of hexahydrated strontium iodate, and at 100°, 0·73 grms. C. F. Rammelsberg's values are about 25 per cent. higher. The solubility of barium iodate has been determined by J. L. Gay Lussac, C. F. Rammelsberg, P. Kremers, and by M. Trautz and A. Anschütz. The last give for the cryohydric or eutectic temp. −0·046° ±0·002°, and with monohydrated barium iodate as solid phase:

	−0·046°	10°	20°	40°	60°	80°	99·2°
Per cent. $Ba(IO_3)_2$.	0·008	0·014	0·022	0·041	0·074	0·115	0·197

W. D. Harkins and W. J. Winninghoff have measured the effect of various salts on the solubility of barium iodate. The b.p. of the sat. soln. at 735 mm. is 99·2°. The soln. in cold hydrochloric acid decomposes. Barium iodate is slightly soluble in warm nitric acid, and, according to W. Eidmann, insoluble in acetone.

The chlorates of beryllium, magnesium, zinc, and cadmium.—A. Atterberg[106] did not succeed in making **beryllium chlorate** except in soln., since the liquid decomposed on evaporation. H. Traube measured the mol. soln. vol. of beryllium chlorate, and found that soln. with 1·949, 2·560, and 3·310 per cent. of $Be(ClO_3)_2$ have the respective sp. gr. 1·01101, 1·01493, and 1·01947 at 15°; and the respective soln. vol. 69·9, 69·3, and 70·2. By evaporating an aq. soln. of magnesium chlorate—from potassium chlorate and magnesium fluosilicate (J. J. Berzelius); or barium chlorate and magnesium sulphate (A. Wächter)—over sulphuric acid, A. Wächter[107] obtained crystals of **hexahydrated magnesium chlorate,** $Mg(ClO_3)_2.6H_2O$, which A. Meusser says melt at 35°, and A. Wächter at 40°. The crystals decompose into water, oxygen, chlorine, and a residual magnesium oxide, at 120°, and if slowly heated, some magnesium chloride as well. The crystals dissolve with difficulty in alcohol, and, according to W. Eidmann, they are soluble in acetone. At 35°, the hexahydrated chlorate passes into **tetrahydrated magnesium chlorate,** $Mg(ClO_3)_2.4H_2O$, crystallizing in hygroscopic rhombohedra. At 65°, the hexa- or tetra-hydrate forms **dihydrated magnesium chlorate,** $Mg(ClO_3)_2.2H_2O$, and the product can be dried at 70° on a porous tile over sulphuric acid; at 80°, the dihydrate slowly decomposes, forming a basic salt, and hence anhydrous magnesium chlorate has not been prepared. A. Meusser gives the solubilities at different temp.:

	−18°	0°	18°	35°	65·5°	68°	[illegible]
Per cent. $Mg(ClO_3)_2$	51·64	53·27	56·50	63·65	69·12	70·69	73·71
Solid phase	$Mg(ClO_3).6H_2O$		$Mg(ClO_3)_2.4H_2O$		$Mg(ClO_3)_2.2H_2O$		

At −12° ice is the solid phase when the soln. has 26·35 per cent. of $Mg(ClO_3)_2$; and at −8°, 22·24 per cent. According to F. Mylius and R. Funk, the sat. soln. at −18° has 128·6 grms. $Mg(ClO_3)_2$ per 100 grms. of water, or 56·3 per cent. $Mg(ClO_3)_2$; and this soln. has a sp. gr. 1·594.

Zinc chlorate, $Zn(ClO_3)_2$, was formed by L. N. Vauquelin in 1815[108] by the action of chloric acid on zinc carbonate; by O. Henry, by the action of zinc fluosilicate on potassium chlorate; and by A. Wächter by the action of barium chlorate on zinc sulphate. The aq. soln. furnishes monoclinic crystals of **hexahydrated zinc chlorate,** $Zn(ClO_3)_2.6H_2O$, which melt at 60°, and decompose into water, chlorine, and oxygen at high temp. These crystals pass into **tetrahydrated zinc chlorate,** $Zn(ClO_3).4H_2O$, at 14·5° to 15°, which melts at 55°; after standing some days at 65°, A. Meusser found that tetrahydrated zinc chlorate passes into **dihydrated zinc chlorate,** $Zn(ClO_3)_2.2H_2O$. The sp. gr. of the soln. of tetrahydrated zinc chlorate at 18° is 1·916. The solubility per 100 grms. of soln. is:

	18°	0°	8°	15°	18°	30°	40°	55°
Per cent. $Zn(ClO_2)_2$	55·62	59·19	60·20	67·32	66·52	76·66	66·06	75·44
Solid phase		$Zn(ClO_3)_2.6H_2O$				$Zn(ClO_3)_2.4H_2O$		$Zn(ClO_3)_2.2H_2O$

When the solid phase is ice at −13°, the soln. has 30·27 per cent. of $Zn(ClO_3)_2$, and at −9°, 26·54 per cent. F. Ephraim and A. Jahnsen have prepared the ammoniates, **zinc tetrammino-chlorate,** $Zn(ClO_3)_2.4NH_3$, in colourless crystals of sp. gr. 1·84, mol. vol. 163·2, with the dissociation press. 16 mm. at 114°; 32 mm. at 140°; 50 mm. at 165°; and 88 mm. at 177°. A. Jahnsen's value for the heat of formation is 17·5 Cals. It explodes at 205° in an open tube and at 289° in a closed tube; it also detonates when struck with a hammer. On exposing the powder to air for about five days, it loses one-fourth of the combined ammonia, and the lost ammonia is readily replaced by water, forming **zinc aquo-triammino-chlorate,**

$Zn(ClO_3)_2.H_2O.3NH_3$. **Zinc hexammino-chlorate,** $Zn(ClO_3)_2.6NH_3$, has a dissociation press. of 225 mm. at $-15°$; 270 mm. at $-10°$; 388 mm. at $-2°$; 427 mm. at 0°; 550 mm. at 6°; 690 mm. at 10°; and 747 mm. at 11°. The heat of formation is 9·8 Cals.

In 1843, A. Wächter made deliquescent prismatic crystals of **dihydrated cadmium chlorate,** $Cd(ClO_3)_2.2H_2O$, which melted at 80°, gave off water, oxygen, and chlorine, and left a residual oxychloride. A. Meusser says that the solid phase between $-20°$ and 65° is dihydrated cadmium chlorate, and that sat. aq. soln. at $-20°$ have 72·18 per cent. of $Cd(ClO_3)_2$; at 0°, 74·95 per cent.; at 18°, has 76·36 per cent.; at 49°, 34·82 per cent.; and at 65°, 82·95 per cent. of $Cd(ClO_3)_2$. F. Mylius and R. Funk find that the sat. soln. at 18° has a sp. gr. of 2·284. F. Ephraim and A. Jahnsen obtained colourless crystals of **cadmium hexammino-chlorate,** $Cd(ClO_3)_2.6NH_3$, of sp. gr. 1·78, and dissociation press. 89 mm. at 69°, 241 mm. at 94°, 530 mm. at 116·5°, and 772 mm. at 122°. It explodes in an open tube at 184°, and in a closed tube at 300°. It also detonates by percussion. **Cadmium tetrammino-chlorate,** $Cd(ClO_3)_2.4NH_3$, has a dissociation press. of 117 mm. at 116·5°, and 335 mm. at 136°. The heat of formation of the hexammino-salt is 14·1 Cals., and of the tetrammino-salt, 15·4 Cals.

The bromates of beryllium, magnesium, zinc, and cadmium.—J. C. G. de Marignac (1873)[109] tried to make *beryllium bromate*, but obtained nothing better than indefinite sticky masses. C. Löwig[110] made a soln. of magnesium bromate by dissolving the oxide or carbonate in bromic acid; and J. Sarghel by the electrolysis of a soln. of magnesium bromide. The crystals of **hexahydrated zinc bromate,** $Zn(BrO_3)_2.6H_2O$, said C. F. Rammelsberg, are regular octahedra; and, according to M. Trautz and P. Schorigin, show triboluminescence. The crystals effloresce in air, and melt in their own water of crystallization, which is lost at about 200°, and at a little higher temp., oxygen and bromine are given off and a residue of magnesium oxide remains. According to C. F. Rammelsberg, 100 grms. of cold water dissolve 0·714 grms. of the salt. C. F. Rammelsberg made similar crystals of what he regarded as **trihydrated zinc diammino-bromate,** $Zn(BrO_3)_2.2NH_3.3H_2O$, or rather as $NZn_2.BrO_3.3NH_4BrO_3.6H_2O$; and F. Ephraim and A. Jahnsen made colourless crystals of **zinc tetramino-bromate,** $Zn(BrO_3)_2.4NH_3$, which explodes in an open tube at 169°, and in a closed tube at 159°; it also detonates by percussion. The sp. gr. of the salt is 2·27; its mol. vol. 171·5; and its heat of formation 16·1 Cals. C. F. Rammelsberg made monoclinic crystals of **monohydrated cadmium bromate,** $Cd(BrO_3)_2.H_2O$, with the axial ratios $a:b:c=1·095:1:0·7298$, $\beta=103° 28'$. The solubility in 100 grms. of water is 125 grms. H. Topsöe has also described rhombic crystals of **dihydrated cadmium bromate,** $Cd(BrO_3)_2.2H_2O$, of sp. gr. 3·758, and axial ratios $a:b:c=1:0·98845:0·7392$. C. F. Rammelsberg also prepared what he regarded as *cadmium triammino-bromate,* $Cd(BrO_3)_2.3NH_3$, but which is probably the **cadmium tetrammino-bromate,** $Cd(BrO_3).4NH_3$, of F. Ephraim and A. Jahnsen, which exploded in open tubes at 192°, and in closed tubes at 193°; it also detonates by percussion. Its sp. gr. is 2·53, mol. vol. 172·4, and its heat of formation 16·9 Cals.

Iodates of beryllium, magnesium, zinc, and cadmium.—J. C. G. de Marignac[111] succeeded only in making indefinite sticky masses when he attempted to prepare *beryllium iodate.* N. A. E. Millon[112] made a soln. of the salt in 1843, and when evaporated at 40°–50°, it furnishes monoclinic prisms of **tetrahydrated magnesium iodate,** $Zn(IO_3)_2.4H_2O$, with a sp. gr., according to F. W. Clarke, of 3·3 at 13·5°; and, according to J. C. G. de Marignac, axial ratios $a:b:c=1·249:1:1·268$; $\beta=100° 40'$. The crystals lose most of their water at about 150°, and almost all at 180°. Magnesium oxide remains when the iodate is heated in air. The soln. in dil. sulphuric acid gives a mixture of crystals of iodic acid and magnesium sulphate. When a sat. soln. of the iodate is cooled to 0°, efflorescent rhombic plates of **decahydrated magnesium iodate,** $Mg(IO_3)_2.10H_2O$, are formed. These crystals melt at about 50° to a clear liquid. The dihydrate is virtually insoluble

in water, and the tetrahydrate and decahydrate, according to A. Ditte, have the solubilities:

	0°	20°	30°	50°	0°	20°	63°	100°
Per cent. $Mg(IO_3)_2$.	3·1	10·2	17·4	67·5	6·8	7·7	12·6	19·3
Solid phase . . .	$Mg(IO_3)_2.10H_2O$				$Mg(IO_3)_2.4H_2O$			

The transition point of the tetra- and deca-hydrated iodate is 13°. The sat. soln. at 18° has a sp. gr. 1·078, and contains 6·44 per cent. of salt. Zinc iodate was made by A. Connell[113] in 1831, and by C. F. Rammelsberg and F. Mylius and R. Funk as a crystalline powder, **dihydrated zinc iodate,** $Zn(IO_3)_2.2H_2O$, by the evaporation of aq. soln. The hydrate, according to A. Jahnsen, loses its water at 200°, and it has then a yellowish-brown colour, but no free iodine can be detected in the product. The sp. gr. of the anhydrous iodate is 4·98, and mol. vol. 83·4. When zinc iodate is heated to a higher temp., it gives off oxygen and iodine, some zinc iodide sublimes, and zinc oxide remains as a residue. The solubility of the hydrate in 100 grms. of water is 0·9 at 15°, and 0·13 at 100°. According to F. Mylius and R. Funk, there is an easily soluble modification. C. F. Rammelsberg also prepared an ammino-derivative, $3Zn(IO_3)_2.8NH_3$; and A. Ditte and F. Ephraim and A. Jahnsen, **zinc tetrammino-iodate,** $Zn(IO_3).4NH_3$, in white needles, sp. gr. 2·82, mol. vol. 171·4, and dissociation press. 44 mm. at 77°; 141 mm. at 106·5°; 356 mm. at 130°. The heat of formation is 15 Cals. The mol. vol. of each NH_3 in the complex is 22. The compound does not explode in an open tube, but in a closed tube it explodes between 210° and 219°. A higher ammino-salt has not been made. A. Ditte (1890) and C. F. Rammelsberg (1842) obtained crystals of **monohydrated cadmium iodate,** $Cd(IO_3)_2.H_2O$. It is easily soluble in water, nitric acid, and ammonia. According to A. Jahnsen, the hydrate loses its water, forming the anhydrous salt at 160°, the product is pale brown, but no free iodine can be detected; its sp. gr. is 6·43, and mol. vol. 71·3. A. Ditte and C. F. Rammelsberg obtained evidence of the formation of an ammoniate, and F. Ephraim and A. Jahnsen made **cadmium tetrammino-iodate,** $Cd(IO_3)_2.4NH_3$, of sp. gr. 3·23, mol. vol. 164·2, and dissociation press. 381 mm. at 91°, 486 mm. at 101°, and 709 mm. at 110°. It explodes like the corresponding zinc compound. The heat of formation is 13·7 Cals. The mol. vol. of each NH_3 in the complex is 17·1.

Mercury chlorates, bromates, and iodates.—L. N. Vauquelin[114] prepared mercurous chlorate, $HgClO_3$, by the action of chloric acid on mercurous oxide; and A. Wächter (1843) and I. Traube (1895) made the same salt in an analogous manner. The crystals are white or greenish-white; those obtained by the evaporation of the soln. at 80° are white rhombic prisms. According to I. Traube, a 0·994 per cent. soln. at 15° has a sp. gr. 1·00802, and the salt has a molecular soln. volume of 36·9; and the 2·791 per cent. soln. a sp. gr. 1·02412, and molecular soln. volume of 36·1; the molecular depression of the f.p. of a 1·016 per cent. soln. is 34·5. The salt is soluble in water, alcohol, and acetic acid; hydrochloric acid precipitates the mercury quantitatively as mercurous chloride. It detonates when heated to about 250°, giving oxygen and a mixture of mercuric oxide and chloride. L. N. Vauquelin also obtained crystals of a **basic mercuric chlorate,** $2HgO.Cl_2O_5.H_2O$, that is, $Hg(ClO_3)_2.Hg(OH)_2$, or $Hg(ClO_3)OH$, by dissolving mercuric oxide in chloric acid, and subsequent evaporation of the soln. If the soln. be evaporated over sulphuric acid, bipyramidal rhombic crystals with the axial ratios $a:b:c = 0·7974:1:0·64595$ are obtained isomorphous with the corresponding bromate. The sp. gr. is 5·15 (H. Topsöe)[115] and 4·998 (H. G. F. Schröder). The crystals deliquesce in air, and redden litmus; they decompose in contact with water, with the separation of mercuric oxide and an acid salt; when triturated with sodium chloride, red mercuric oxychloride is formed. Conc. sulphuric acid produces flashes of light. When heated, this salt decomposes into mercury, mercurous and mercuric chlorides, and oxygen. According to J. D. Riedel, unlike one per cent. soln. of mercuric chloride, 1 to 2 per cent. soln. of this salt give no precipitate with soln. of white of

egg, or blood serum. A mixture of this salt with tannin albuminate is sold as *mergal* and used in syphilitic diseases.[116]

C. Löwig[117] and C. F. Rammelsberg prepared **mercurous bromate,** $HgBrO_3$, as a yellowish-white powder, by treating a soln. of mercurous nitrate with bromic acid or potassium bromate. It crystallizes from an excess of acid in thin plates. When treated with hot water, mercurous bromate becomes citron yellow and forms basic mercurous bromate, $2Hg_2O.Br_2O_5$, that is, $Hg_2O.2HgBrO_3$; the acid liquid gives on evaporation needle-like crystals of mercuric bromate, $Hg(BrO_3)_2$. Mercurous bromate is not very soluble in nitric acid; and with hydrochloric acid it forms mercuric chloride. The basic salt is also formed as a by-product in the preparation of hypobromous acid from bromine water and mercuric bromide. Basic mercurous bromate becomes grey when exposed to light; it is transformed to normal mercurous bromate when treated with a little nitric acid, and it dissolves when treated with more acid.

C. Löwig obtained **mercuric bromate** by the action of bromine water on mercuric oxide, and after evaporation to dryness extracting the mercuric bromide with alcohol. If a neutral soln. of mercuric nitrate, as hot as possible, be treated with potassium bromate, crystals of **basic mercuric bromate,** $2HgO.Br_2O_5.H_2O$—that is, $Hg(BrO_3)_2.Hg(OH)_2$, or $Hg(BrO_3)OH$—are formed, provided the liquid does not contain too much free nitric acid; if it does, a double salt with mercuric nitrate is formed. Again, according to H. Topsöe, if two mol. of precipitated mercuric oxide be digested for some hours with three mol. of bromic acid, and the liquid be poured from the undissolved oxide bipyramidal rhombic plates of basic mercuric bromate with axial ratios—$a:b:c=0{\cdot}7997:1:0{\cdot}6278$. The sp. gr. is 5·815. The crystals are soluble in dil. acids, and slowly decomposed by cold water, forming a more basic yellow product; they are completely decomposed by boiling water, and the acid or normal salt passes into soln. C. F. Rammelsberg obtained **dihydrated mercuric bromate,** $Hg(BrO_3)_2.2H_2O$, as a white powder by evaporating the acid liquid obtained by treating yellow mercuric oxide with bromic acid; it is obtained in small crystals by cooling the boiling aq. soln. The solubility of the salt in 100 grms. of water is 0·154 grm. in cold water, and 1·56 grms. in boiling water. It decomposes when heated to 130° or 140°. It is decomposed by hydrochloric acid; soln. of alkali iodides turn the salt brown without dissolution. It is soluble in nitric acid.

In 1815, L. N. Vauquelin[118] precipitated **mercurous iodate,** $HgIO_3$, from a soln. of mercurous nitrate by the addition of iodic acid or alkali iodate. The precipitation does not occur if too much free acid is present. A. Ditte noted the formation of a mixture of mercurous iodide and iodate during the action of aq. iodic acid on mercury, an action which proceeds slowly at ordinary temp., but rapidly if heated. Mercurous iodate volatilizes at 250°, forming mercuric iodide, mercury, and oxygen. Mercurous iodate is sparingly soluble in water; boiling water does not act on the salt; it is soluble in iodic acid; cold nitric acid has no action; hot nitric acid gives red vapours, and forms mercuric iodate, $Hg(IO_3)_2$; and hydrochloric acid forms mercuric chloride.

C. F. Rammelsberg[119] made **mercuric iodate,** $Hg(IO_3)$, by treating freshly precipitated mercuric oxide with an excess of warm iodic acid; red mercuric oxide is scarcely affected by this treatment. A. Pleischl, and C. F. Rammelsberg, said that iodic acid and the alkali iodates give no precipitate with mercuric salts, but N. A. E. Millon, and C. A. Cameron state this applies only to mercuric chloride, not mercuric nitrate, acetate, or oxycyanide, for soln. of these salts furnishes a precipitate of mercuric iodate under these conditions: $HgO.HgCy_2+2HIO_3=HgCy_2+H_2O+Hg(IO_3)_2$. N. A. E. Millon also made the same salt by heating a mixture of mercuric chloride and iodic acid in a metal bath until iodine chloride begins to be evolved. The residue is washed with water and alcohol. According to K. Kraut, when mercuric iodide is boiled with nitric acid of sp. gr. 1·5, mercuric iodate is formed; with an acid of sp. gr. 1·4, the product is contaminated with a little

nitrate; with an acid of sp. gr. 1·3 micaceous crystals of $HgI_2.Hg(HO_3)_2$ are formed; and with an acid of sp. gr. 1·2, a mixture of unaltered iodide and the double compound is formed. C. A. Cameron obtained no reaction by heating a mixture of potassium chlorate, mercuric iodide, and water in a sealed tube at 170°, but at 200°, potassium iodide and mercuric chloride was formed. Heat converts mercuric iodate to iodide with the evolution of oxygen. Mercuric iodate is soluble in hydrochloric, hydrobromic, or hydriodic acid with decomposition; it dissolves in soln. of the alkali chlorides, bromides, or iodides—in the cold, one mol. of the iodate dissolves in the presence of four mol. of alkali iodide, and with a boiling soln., in two mol. It is also soluble in soln. of alkali cyanides and thiosulphates and in dil. soln. of zinc or manganous chloride. During evaporation of soln. in potassium chloride, ammonium chloride, or sodium iodide, alkali iodate first separates, then follows the mercuric halide with a number of crystalline double salts or mixed crystals. Mercuric iodate not soluble in soln. of ammonia; alkali, hydroxides, iodates, chlorates, bromates, or sulphites; in mercuric chloride; sodium phosphate; borax; acetic, hydrofluoric, or hydrofluosilicic acid.

The halogenates of aluminium, scandium, thallium, and the rare earths.—J. J. Berzelius obtained what appeared to be aluminium chlorate by treating aluminium fluosilicate with a hot conc. soln. of potassium chlorate; and E. Schlumberger[120] obtained a soln. of the chlorate mixed with alum by treating potassium chlorate with aluminium sulphate. D. K. Dobroserdoff found that when the soln. prepared by the interaction of barium chlorate and aluminium sulphate is evaporated over sulphuric acid, it deposits hygroscopic crystals of **enneahydrated aluminium chlorate,** $Al(ClO_3)_2.9H_2O$, from cold soln., and of **hexahydrated aluminium chlorate,** $Al(ClO_3)_2.6H_2O$, from hot soln. The anhydrous salt has not been obtained on account of its ready decomposibility. The salt explodes at 100° if slowly heated owing to the evolution of chlorine dioxide; if rapidly heated there is no explosion and chlorine is evolved, and a basic perchlorate remains. C. F. Rammelsberg (1842)[121] attempted to make aluminium bromate by evaporating a soln. of aluminium hydroxide in bromic acid, but obtained only a sticky mass. D. K. Dobroserdoff prepared **enneahydrated aluminium bromate,** $Al(BrO_3)_3.9H_2O$, as in the case of the corresponding chlorate. The crystals melt at 62·3°, and cannot be dehydrated without decomposition. At 100°, a red, hygroscopic mass is formed, probably a mixture of bromate, perbromate, and oxide. **Aluminium iodate** has not been examined. A. Ditte noted that a conc. soln. of iodic acid slowly dissolves the metal.

W. Crookes[122] found that when an aq. soln. of chloric acid is sat. with scandium hydroxide, a clear colourless soln. of **scandium chlorate** is formed, which is decomposed when evaporated on the water-bath, and chlorine is evolved. Needle-like crystals—probably perchlorate—separate when the mother liquid cools, and a gummy mass remains which, after standing some time, gives another crop of needle-like crystals. When a soln. of scandium hydroxide in bromic acid is evaporated the **scandium bromate** decomposes, and an amorphous gummy mass remains. W. Crookes prepared **octodeca-hydrated scandium iodate,** $Sc(IO_3)_3.18H_2O$, by treating a soluble scandium salt with ammonium iodate. The white crystalline powder is almost insoluble in water but soluble in nitric acid. When kept for some time in a desiccator it forms **pentadeca-hydrated scandium iodate,** $Sc(IO_3)_3.15H_2O$; when dried for several hours in vacuo over sulphuric acid, it forms **trideca-hydrated scandium iodate,** $Sc(IO_3)_3.13H_2O$; when heated for some hours at 100°, it forms **decahydrated scandium iodate,** $Sc(IO_3)_3.10H_2O$; and when heated to about 250°, it loses all its water of crystallization, forming anhydrous **scandium iodate,** $Sc(IO_3)_3$.

The rare earths furnish soluble chlorates and bromates, and sparingly soluble iodates. The chlorates and bromates of the rare earths were prepared by C. F. Rammelsberg and J. C. G. de Marignac by covering barium bromate with water on a water-bath, and gradually adding with constant stirring the neutral rare earth sulphate. The barium sulphate is removed by filtration, and the bromate

crystallized from the soln. The iodates are likewise prepared by double decomposition. Erbium and yttrium form respectively **octohydrated erbium chlorate,** $Er(ClO_3)_3.8H_2O$, and **octohydrated yttrium chlorate,** $Yt(ClO_3)_3.8H_2O$. The latter was made by P. T. Cleve[123] and O. Popp, and forms deliquescent white needle-like crystals. The corresponding bromates are **enneahydrated erbium bromate,** $Er(BrO_3)_3.9H_2O$, and **enneahydrated yttrium bromate,** $Yt(BrO_3)_3.9H_2O$. Yttrium enneaquobromate was prepared by P. T. Cleve in needle-like crystals slightly soluble in ether, and readily soluble in alcohol. According to C. James and W. T. Langlier, this salt melts at 74°, and 100 parts of water at 25° dissolve 128 parts of the salt. At 100°, **trihydrated yttrium bromate,** $Yt(BrO_3)_3.3H_2O$, is formed. **Ytterbium bromate** has also been made. **Enneahydrated lanthanum bromate,** $La(BrO_3)_3.9H_2O$, was described by C. F. Rammelsberg, J. C. G. de Marignac, and R. Hermann. It forms hexagonal prisms, which, according to C. James and W. T. Langelier, melt at 37·5°, and 416 parts of the hydrated salt dissolve in 100 parts of water at 25°. When dried at 100°, this salt forms **dihydrated lanthanum bromate,** $La(BrO_3)_3.2H_2O$; the anhydrous salt is formed at 150°; and at higher temp., the salt decomposes. J. C. G. de Marignac prepared **enneahydrated didymium bromate,** $Di(BrO_3)_3.9H_2O$, in rose-red hexagonal prisms with the axial ratio $a:c=1:0·5731$, and, according to A. des Cloizeaux, with negative double refraction. According to C. James and W. T. Langelier, green hexagonal prisms of **enneahydrated praseodymium bromate,** $Pr(BrO_3)_3.9H_2O$, melt about 56·5°, and 100 parts of water dissolve 190 parts of the hydrated salt at 25°; it forms **dihydrated praseodymium bromate,** $Pr(BrO_3)_3.2H_2O$, at 100°; it becomes anhydrous at 130°; and decomposes at 150°. Pink hexagonal prisms of **enneahydrated neodymium bromate,** $Nd(BrO_3)_3.9H_2O$, melt at about 66·7°, and 100 parts of water at 25° dissolve 146 parts of the hydrated salt; it forms **dihydrated neodymium bromate,** $Nd(BrO_3)_3.2H_2O$, at 100°; it becomes anhydrous at 150°; and decomposes at higher temp.; yellow hexagonal prisms of **enneahydrated samarium bromate,** $Sm(BrO_3)_3.9H_2O$, melts at 75°, and 100 parts of water at 25° dissolve 114 parts of the hydrated salt. This salt forms **dihydrated samarium bromate,** $Sm(BrO_3)_3.2H_2O$, at 100°; the anhydrous salt at 150°; and it decomposes at higher temp. **Enneahydrated cerium bromate,** $Ce(BrO_3)_3.9H_2O$, is crystallized from aq. soln. by concentration in vacuo at 35°, and then cooling. The salt melts at 49°, and decomposes at a rather higher temp. Pale yellow hexagonal needles of **enneahydrated dysprosium bromate,** $Dy(BrO_3)_3.9H_2O$, melting at 78°, were prepared by G. Jantsch and A. Ohl; when heated for some time at 110°, **trihydrated dysprosium bromate,** $Dy(BrO_3)_3.3H_2O$, is formed. Pale bluish-green hexagonal prisms of **enneahydrated thulium bromate,** $Tm(BrO_3)_3.9H_2O$, have also been made. All these salts, $M(BrO_3)_3.9H_2O$, crystallize in hexagonal prisms, and they are all converted into tetrahydrated salts at 100°; and with the exception of praseodymium bromate, are converted into the anhydrous at 130°—praseodymium bromate decomposes at 130°. The order of increasing solubility of the bromates is: samarium (europium, gadolinium), terbium, dysprosium, holmium, yttrium, erbium, thulium, and ytterbium. C. James utilizes this property for the fractional separation of some of these elements.

Cerous iodates and the iodates of the other rare earths form crystalline salts sparingly soluble in water, but readily soluble in conc. nitric acid, and in this respect differ from the ceric, zirconium, and thorium iodates, which are almost insoluble in nitric acid when an excess of a soluble iodate is present. It may also be noted that cerium alone of all the rare earth elements is oxidized to a higher valence by potassium bromate in nitric acid soln. The iodates of the rare earths are precipitated by adding an alkali iodate to the rare earth salts, and the fact that the rare earth iodates are soluble in nitric acid, and the solubility increases as the electro-positive character of the element increases, while thorium iodate is insoluble in nitric acid, allows the method to be used for the separation of these elements. **Trihydrated erbium iodate,** $Er(IO_3)_3.3H_2O$, and **trihydrated yttrium iodate,** $Yt(IO_3)_3.3H_2O$,

were made by P. T. Cleve as pulverulent precipitates by adding iodic acid to salts of the respective elements. 100 grms. of water dissolve 0·53 grms. of yttrium iodate; when heated, this salt decomposes explosively. A. Cleve precipitated **hexahydrated ytterbium iodate,** $Yb(IO_3)_3.6H_2O$, as a snow-white powder on adding iodic acid to ytterbium acetate. It forms ytterbium dihydrated iodate, $Yb(IO_3)_3.2H_2O$, when dried at 100°. P. T. Cleve, and R. Hermann described **trihydrated lanthanum iodate,** $La(IO_3)_3.3H_2O$—M. Holzmann regards it as $2La(IO_3)_3.3H_2O$—as a white crystalline precipitate but sparingly soluble in cold water, and which crystallizes in plates on cooling its soln. in boiling water. According to E. Rimbach and A. Schubert, a litre of soln. sat. at 25° contains 1·87 grms. of the anhydrous iodate. P. T. Cleve prepared **hexahydrated samarium iodate,** $Sm(IO_3)_3.6H_2O$, as a gelatinous precipitate which becomes anhydrous at 100°. The chlorates, bromates, and iodates of gallium and indium have not been closely examined.

F. C. Mathers and C. G. Schlüderberg[124] prepared **indium iodate,** $In(IO_3)_3$, by mixing soln. of indium trichloride and potassium iodate. The precipitate is amorphous. The mixture was evaporated to dryness on a water-bath; the residue extracted on a Gooch's crucible with warm water; and dried in vacuo over sulphuric acid. The mass was dissolved in boiling nitric acid (1 : 10), and on evaporation white crystals of indium iodate were formed. 100 grms. of water at 20° dissolve 0·067 grm., and 100 grms. of nitric acid (1 : 5) at 80° dissolve 0·67 grm. of the salt. It also dissolves in dil. sulphuric or hydrochloric acid. The soln. in the last-named acid decomposes with the liberation of chlorine. The crystals decompose with the evolution of iodine when heated by a free flame; and explode if touched with a red-hot iron wire.

Thallous chlorate, $TlClO_3$, is formed by dissolving the metal in chloric acid; or by mixing soln. of potassium chlorate and thallous nitrate, or, as recommended by J. Muir, by mixing soln. of barium chlorate and thallous sulphate.[125] The needle-like crystals, says J. W. Retgers, are isomorphous with potassium chlorate—isodimorphous, according to H. W. B. Roozeboom. The sp. gr. is 5·5047 at 9°. Like potassium chlorate, it is sparingly soluble in cold water but readily soluble in hot water; according to J. Muir, 100 grms. of water dissolve:

	10·5°	13·8°	18·5°	24·8°	30·9°	47·6°	56·6°	81·5°
$KClO_3$ . . .	2·83	2·99	3·71	5·04	6·25	10·56	16·52	32·79 grms.

These values are covered by J. Muir's formula, $S=1·99+0·05415\theta+0·00139\theta^2+0·000036\theta^3$. According to E. Franke, the eq. conductivity when v denotes the number of litres of water containing a mol. of the salt is 123·6 when $v=32$; 132·1 when $v=256$; and 135·4 when $v=1024$. When heated, thallic perchlorate is formed. **Thallous bromate,** $TlBrO_3$, was made by P. S. Oettinger (1864),[126] and by A. Ditte (1890), and hot soln. furnish on cooling small, white, needle-like crystals which are readily soluble in dil. acids. According to W. Böttger, a litre of water dissolves 0·009948 mol. at 19·94°—*i.e.* 0·3463 grms. per 100 c.c.—and 0·02216 at 39·75°; the degree of ionization is between 89 and 90·2. The eq. conductivity at a dilution, $v=128$, is 122·9; heated in a dry tube, it decomposes with a feeble detonation, forming thallous oxide; at 100°, it is reddened, then blackened, and becomes insoluble in water. **Thallous iodate,** $TlIO_3$, was prepared by P. S. Oettinger[127] in 1864 in needle-like crystals, sparingly soluble in water, and slightly soluble in nitric acid. According to W. Böttger, 100 grms. of water at 19·95° dissolve 0·058 grm. of $TlIO_3$, or 0·00152 mol. per litre. The electrical conductivity for $v=512$ is 111·5, and for $v=1024$, 112·0. According to A. Ditte, if the crystals separate from the soln. below 30°, they are **hemihydrated thallous iodate,** $TlIO_3.\frac{1}{2}H_2O$. C. F. Rammelsberg also made a **basic thallic iodate,** $Tl_2O_3.2I_2O_5.3H_2O$, by the action of iodic acid on thallic hydroxide. The greyish-brown crystals are decomposed by alkali lye; soluble in hot dil. sulphuric acid; lose water at about 190°.

The halogenates of tin and lead.—The chlorates of tin are ill-defined. According

to A. Wächter,[128] freshly precipitated stannous hydroxide dissolves in chloric aci forming a soln. of what is possibly **stannous chlorate,** which, in a few minutes, deto ates and leaves a residue containing free chloric acid, stannic hydroxide, and stann chloride. If stannous chloride be triturated with half its weight of potassiu *chlorate, the mass becomes hot, and chlorine dioxide is evolved.* When the yello mass is extracted with hot water, and the soln. allowed to crystallize, potassiu chlorate is obtained. Metallic tin, according to W. S. Hendrixson, dissolves chloric acid without the evolution of hydrogen, forming a soln. of **stannic chlorat**

A. Wächter[129] obtained rhombohedral deliquescent crystals of **monohydrate lead chlorate,** $Pb(ClO_3)_2.H_2O$, from hot soln. of chloric acid sat. with lead oxid W. K. Lewis has shown that chloric acid can take up much more lead oxide tha *corresponds with the formation of the normal salt, and on boiling the soln.,* sparingly soluble basic lead chlorate is precipitated. To prepare the normal chlora the calculated quantities of acid and oxide are evaporated to dryness, and tl residue dissolves in very dil. chloric acid. The salt is precipitated as monohydrate lead chlorate, $Pb(ClO_3)_2.H_2O$, by the addition of alcohol. According to J. C. (de Marignac, the monoclinic prisms, with the axial ratios $a:b:c=1.1426:1:1.173($ $\beta=93^\circ 7'$, are isomorphous with the corresponding barium salt. The sa *decomposes when heated either gradually or at an explosive speed.* W. H. Sodea found that the slow decomposition between 190° and 260° progressed by two sic reactions: $Pb(ClO_3)_2=PbCl_2+3O_2$, and $Pb(ClO_3)_2=PbO_2+Cl_2+2O_2$; the latter seven times as fast as the former. If the chlorine in the last-named reaction not rapidly removed from the system, it reacts with the lead dioxide: PbO_2+C $=PbCl_2+O_2$. The explosive reaction which occurs by quickly heating the chlorat to 235° is probably similar, except that an oxychloride is formed in place of tl *dioxide. Mixtures of lead chlorate with oxidizing agents are explosive. Accordir* to F. Mylius and R. Funk, 100 grms. of water at 18° dissolve 151·3 grms. of tl salt, and at 25·3°, 254·7 grms.; the sp. gr. of the sat. soln. are respectively 1·94 and 2·346. A soln. of lead chlorate of sp. gr. 1·164 with 19·13 grms. of $Pb(ClO_3)$ per 100 grms. of water, at 25·3°, dissolves, according to W. K. Lewis, 95·1 grms. ($NaClO_3$, or 5·94 grms. of $KClO_3$ per 100 grms. of water. The sum of individu solubilities with the potassium salt is 263 grms. per 100 grms. of water; the observe *result is 272 grms. This is not sufficient to justify the assumption that any apprec* able amount of the double salt is present in the soln. W. K. Lewis found th potential of $0.01N$-, $0.05N$-, and $0.5N$-lead chlorate soln. with a lead electrod against a normal electrode to be respectively −0·463, −0·450, and −0·431 volt a 25°; the addition of the eq. $0.05N$-sodium potassium chlorate gives a potenti respectively of −0·461 and −0·460 volt.

C. F. Rammelsberg[130] obtained monoclinic prisms of **monohydrated lea bromate,** $Pb(BrO_3)_2.H_2O$, with axial ratios $a:b:c=1.1621:1:1.2092$; $\beta=87^\circ 32$ and of sp. gr. 1·33 at 15°–18°, and isomorphous with monohydrated strontiu bromate. The salt decomposes at 180°, forming lead dioxide and bromide, an bromine; at higher temp. red lead, bromine, and lead bromide are formed. . sat. soln. at 19·94° has 13·4 grms. or 0·0289 mol. per litre, and the soln. is 72 per cen ionized. D. Strömholm reported the formation of **basic lead bromat** $3PbO.Pb(BrO_3)_2.2H_2O$, by the action of ammonium bromate on lead hydroxide he also reported an analogous **basic lead iodate.** Normal **lead iodate,** $Pb(IO_3)$ was made by C. F. Rammelsberg as a sparingly soluble precipitate by adding a alkali iodate or iodic acid to a soln. of lead nitrate. According to W. D. Harkir and W. J. Winninghoff, water at 25° dissolves 0·0001102 eq., or 0·0307 grm. (lead iodate per litre. F. Kohlrausch calculates the following solubilities, in gram-e per litre, from the specific conductivities:

	9·17°	17·1°	18°	25·77°
Specific conductivity $\times 10^6$	3·58	5·67	5·96	9·14
Solubility $\times 10^5$	4·80	6·21	6·39	8·25

There is a decrease in the solubility of a sat. soln. with time.

The halogenates of zirconium, cerium, and thorium.—M. Weibull[131] claimed to have obtained needle-like crystals of **hexahydrated zirconyl chlorate,** $ZrO(ClO_3)_2.6H_2O$, by the double decomposition of barium chlorate and zirconium sulphate, $Zr(SO_4)_2$, and the evaporation of the soln. over potassium hydroxide. F. P. Venable and I. W. Smithey prepared the salt by treating a soln. of zirconium perchlorate with potassium chlorate. When the soln. is conc. by evaporation, crops of crystals of potassium perchlorate separate out, and finally the yellow syrupy mother liquor, smelling of chlorine monoxide, furnishes crystals of zirconium chlorate which give on analysis $ZrO(OH)_2.3ZrO(ClO_3)_2$. The normal salt is not obtained because it is hydrolyzed. The salt is very deliquescent; very soluble in water; soluble in alcohol; and insoluble in ether. The crystals had a yellow tinge and they oxidized organic matter. The *zirconyl bromate* has not been investigated. What is probably **zirconyl iodate** is precipitated quantitatively from neutral or slightly acid soln. of a zirconium chloride by the addition of an excess of alkali iodate or iodic acid. A white curdy precipitate forms immediately, it redissolves on stirring, but with further additions of the precipitant, the precipitate becomes permanent. It settles quickly, and can be washed by decantation. G. A. Barbieri prepared **ceric iodate,** $Ce(IO_3)_4$, by heating cerous nitrate iodic acid and conc. nitric acid. The yellow crystalline solid is very sparingly soluble in boiling nitric acid, and is hydrated by water. Thorium, zirconium, and ceric iodates are not very soluble in water, and almost insoluble in nitric acid, provided an excess of iodate ions be present. According to F. P. Venable and I. W. Smithey, zirconyl iodate forms a white powder, insoluble in water, alcohol, and ether; it is decomposed by conc. hydrochloric acid with the evolution of chlorine; and it showed signs of decomposition at 100°, and iodine vapours are visible at 125°. Analyses of samples prepared under different conditions, and dried at room temp., have a variable composition between $Zr_3O_4(IO_3)_4$ and $Zr_4O_7(IO_3)_2$. The normal salt, $ZrO(IO_3)_2$, has not been obtained because the salt is so readily hydrolyzed by water; it is far more readily hydrolyzed than the chlorate; **thorium iodate** is precipitated like the iodates of cerium and zirconium. All three iodates decompose when calcined, forming ZrO_2, CeO_2, or ThO_2, as the case might be. R. J. Meyer and M. Speter have developed a method for the separation of thorium from the rare earths and cerium by precipitation as thorium iodate, for the rare earth and cerous iodates are soluble in nitric acid; P. H. M. P. Brinton and C. James likewise separated cerium from the rare-earth group by precipitation as ceric iodate; and J. T. Davis used a similar process for the analogous separation of zirconium.

The salt **enneahydrated cerous bromate,** $Ce(BrO_3)_3.9H_2O$, was obtained by C. F. Rammelsberg[132] by double decomposition between barium bromate and cerous sulphate. It forms colourless hexagonal prisms which melt at 49°, and decompose just above this temp., and this even in aq. soln. In this respect it differs from the rare earths with which it is usually accompanied, and C. James suggests that this property can therefore be utilized for purifying the salt. **Dihydrated cerous iodate,** $Ce(IO_3)_3.2H_2O$, is precipitated when alkali iodate or iodic acid is added to cerium salts. Like the iodates of the rare earths, cerous iodate is soluble in nitric acid; it is sparingly soluble in cold water, and is decomposed by prolonged washing; hence M. Holzmann prefers washing with alcohol. Half the water is lost by the hydrated iodate at 110°.

P. T. Cleve[133] prepared **thorium chlorate** by double decomposition of barium chlorate and thorium sulphate, followed by evaporation under reduced press. The resulting soap-like deliquescent mass is very soluble in water. **Thorium bromate** behaved similarly.

The halogenates of chromium, uranium, and manganese.—The double decomposition of chrome alum and barium chlorate, or a soln. of chromic sulphate and potassium chlorate, furnishes a violet liquid containing **chromium chlorate,**[134] which becomes green at 65°. Even at ordinary temp. the soln. smells of chlorine; at 100°, chlorine gas is given off and the liquid becomes reddish-yellow—it contains chromic

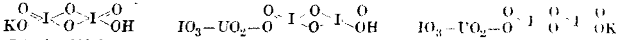
anhydride and oxychlorine compounds—it is a vigorous oxidizing agent. C. F. Rammelsberg evaporated the soln. of **chromium bromate,** obtained by treating chromium sulphate with barium bromate, on a water-bath and found it decomposed in an analogous manner to the corresponding chlorate soln. Crystals of chromic anhydride separated from the conc. soln. N. J. Berlin [135] obtained a dark blue precipitate—**chromium iodate**—by adding sodium iodate to a soln. of chromic chloride; and a similar precipitate is formed when ether or alcohol is added to soln. of chromium iodate. A. Berg prepared a complex acid—*chromatoiodic acid*—*in ruby-red rhombic crystals which are hygroscopic, by the soln. of equimolecular* parts of iodic and chromic acids: $HIO_3.CrO_3.2H_2O$, or

$$\begin{matrix} HO & & O & & O \\ & I & & Cr & \\ O & & O & & O \end{matrix}$$

According to C. F. Rammelsberg,[136] uranium hydroxide forms a green soln. when treated with chloric acid, which rapidly decomposes when warmed, forming a soln. of uranyl *chloride*, UO_2Cl_2. *If a soln. of uranyl sulphate be treated with barium* bromate, C. F. Rammelsberg also obtained a yellow filtrate which decomposed on evaporation over conc. sulphuric acid, bromine is evolved, and a solid mass when redissolved leaves a brown powder as residue. The soln. when evaporated gives a yellow pulverulent substance, probably uranyl bromide, UO_2Br_2. A. Fleischl obtained a white precipitate on treating a soln. of uranyl nitrate with potassium iodate, or iodic acid, and, according to A. Ditte, (i) if the operation is performed with sodium iodate, over 60°, in the presence of an excess of nitric acid, the crystals which form are anhydrous uranyl iodate, $UO_2(IO_3)_2$; the same salt is formed (ii) in the cold by treating uranyl nitrate with iodic acid or an alkali iodate; the pale yellow precipitate soon forms yellow rhombic prisms, which decompose at 250°, giving off iodine and oxygen. The salt formed in the cold (ii) is readily soluble in nitric or phosphoric acid, and it can be recovered in small crystals by the concentration of the soln.; the salt formed at the higher temp. (i) is not soluble in these two acids. Hydrochloric acid decomposes uranyl iodate with the evolution of chlorine. According to C. F. Rammelsberg, the iodate formed by the cold process (ii) in dil. soln. is hydrated, $UO_2(IO_3).5H_2O$. According to P. Artmann, the salt precipitated from nitric acid soln. is really **monohydrated uranyl iodate,** $UO_2(IO_3).H_2O$; it forms rhombic prisms of sp. gr. 5·220 (18°); 100 c.c. of water at 18° dissolves 0·1049 grm. of the salt. It begins to lose iodine at 265°. The same salt is precipitated from boiling soln. in the absence of nitric acid; ammonium iodate or iodic acid in the cold precipitates the same salt from uranyl nitrate soln. Irregular crystal aggregates, of sp. gr. 5·052 (18°), are formed, and 100 c.c. of water at 18° dissolve 0·1214 grm. of the salt. It begins to lose its water at 253°. By boiling the former with water it passes into the latter, and at this temp. 100 c.c. of water dissolve 0·2367 grm. The solubility of the mono-aquo-salt is reduced to 0·0076 grm. per 100 c.c. of solvent in the presence of a sat. soln. of sodium iodate, and to 0·1154 grm. with uranyl nitrate.

Dihydrated uranyl iodate, $UO_2(IO_3)_2.2H_2O$, is obtained by using cold dil. soln. in the absence of nitric acid; or by adding 100 c.c. of conc. sodium iodate gradually to 30 c.c. of a conc. soln. of uranyl nitrate. The precipitate first formed redissolves, and later yields crystals or crystal aggregates of a paler yellow than the mono-aquo salt. When recrystallized from water it forms mono-aquo-salt of sp. gr. 3·911. The diaquo-salt is soluble in water, for 100 c.c. of water at 18° dissolve 0·2044 grm. A boiling soln. of potassium chloride or nitrate decomposes uranyl iodate, forming **uranyl potassium iodate,** $UO_2K(IO_3)_3.3H_2O$, uranyl chloride, and potassium iodate: $2UO_2(IO_3)_2+2KCl=KIO_3+UO_2Cl_2+UO_2K(IO_3)_3$. The salt is also formed as a sparingly soluble yellow powder by precipitation with an excess of potassium iodate. An excess of uranyl nitrate converts this salt into uranyl iodate. The salt is hydrolyzed by water, and 100 c.c. of a sat. soln. of potassium iodide dissolves the eq. of 0·02 grm. UO_2. All the water is lost at 175°, and the

anhydrous salt, $KUO_2(IO_3)_3$, is formed; at 110° it forms the mono-aquo salt $KUO_2(IO_3)_3.H_2O$. P. Artmann regards the potassium salt as being formed by replacing water in $UO_2(IO_3)_2.H_2O$ by KIO_3. He supposes that monohydrated uranyl iodate is related to the bi-iodate, MHI_2O_2, by C. W. Blomstrand's formula:



Potassium bi-iodate. Uranyl mono-aquo-iodate, $UO_2(IO_3)_2.H_2O$. Uranyl potassium iodate $KUO_2(IO_3)_3$

or the doubled formula, $KIO_3.IO_3.UO_2.IO_3.IO_3.UO_2.IO_3.KIO_3$.

A. Wächter [137] found that the colourless soln. of **manganous chlorate,** obtained by double decomposition of barium chlorate and manganous sulphate, decomposes during its evaporation over conc. sulphuric acid when the concentration attains a certain value. The dil. soln. can be boiled, but it is coloured red when treated with dil. sulphuric acid, and a mixed precipitate of manganese dioxide and sulphate is formed by the addition of conc. sulphuric acid. A. Jahnsen treated a cold soln. of manganese chlorate with ammonia, and added alcohol to the filtrate, the yellowish-brown **manganese ammino-chlorate** rapidly darkened by oxidation. C. F. Rammelsberg's attempt to obtain solid **manganous bromate** did not succeed because of the decomposition of the soln. during concentration. A soln. of **manganous iodate,** $Mn(IO_3)_2$, is readily formed by the action of iodic acid on manganous salts; and red crystals of the salt are obtained by mixing hot soln. of an alkali iodate and a manganous salt—*e.g.* manganous acetate; and by the slow evaporation at 60°–70° of mixed soln. of manganous nitrate, alkali iodate, and nitric acid. According to C. F. Rammelsberg, about half a gram of the salt dissolves in 100 grms. of water; A. Ditte says the salt is insoluble in water and in nitric acid. It is decomposed by boiling sulphuric acid. On calcination, iodine and oxygen are given off and manganese oxide remains. A. Berg [138] dissolved manganese dioxide in iodic acid in the presence of manganous iodate and obtained a lilac-brown or violet powder—probably the potassium salt of a complex **mangani-iodic acid,** $2KIO_3.Mn(IO_3)_4$. The ammonium and barium salts have also been prepared.

The halogenates of iron, nickel, and cobalt.—The colourless soln. obtained by the mutual action of ferrous sulphate and barium chlorate probably contains **ferrous chlorate,** but, as A. Wächter [139] has shown, it is very unstable and readily decomposes, giving a brown liquid containing ferric chloride and **ferric chlorate.** Ferric chlorate appears to be formed by the action of chlorine on water with iron oxide in suspension. According to J. Thomsen, the heat of formation is $Fe(OH)_3+3HClO_3+aq.=Fe(ClO_3)_3+3H_2O+32{\cdot}22$ Cals. Octahedral crystals of **ferrous bromate** are obtained by evaporating in vacuo the soln. obtained by dissolving ferrous carbonate in bromic acid. C. F. Rammelsberg has pointed out that potassium bromate gives no precipitate with ferrous chloride, but with ferrous sulphate a reddish-brown precipitate of a basic salt is obtained which dissolves in a large quantity of water, and the soln. smells of bromine. Freshly precipitated ferric oxide dissolves in bromic acid, forming a soln. of **ferric bromate,** but the syrupy liquid obtained by evaporation in vacuo does not crystallize; warm water dissolves part of the mass, leaving a residual basic bromate which is probably a mixture.

A. Connell (1802) [140] obtained a white precipitate—**ferrous iodate**—by boiling a soln. of iron in iodic acid, and C. F. Rammelsberg found that the addition of potassium iodate to ferrous sulphate gives a yellowish-white precipitate which is decomposed when heated. It is sparingly soluble in nitric acid, and it dissolves in an excess of ferrous sulphate, and the soln., when heated, precipitates basic ferric iodate. A. Ditte mixed boiling soln. of a ferric salt and an alkali iodate and obtained a brown precipitate—**ferric iodate**—insoluble in hot nitric acid diluted with its own volume of water. Crystals can be obtained by mixing warm dil. soln. of ferric nitrate, acidified with nitric acid, and sodium iodate. The precipitate

redissolves as fast as it forms, but separates anew on evaporation. The salt is not altered by exposure to air, and is decomposed when heated. If ferrous chloride acidified with nitric acid be boiled with an alkali iodate, a red precipitate of basic iodate, $Fe_2O_3.I_2O_5$, is obtained; with an excess of potassium iodate and iron alum a yellow precipitate, $Fe_2O_3.2I_2O_5.8H_2O$, is formed; this salt turns brown on exposure to air, and gives off iodine. C. F. Rammelsberg has made other basic ferric iodates which may or may not be chemical individuals.

The liquid obtained by double decomposition between cobalt sulphate and barium chlorate furnishes red octahedral cubic crystals of **hexahydrated cobalt chlorate,** $Co(ClO_3)_2.6H_2O$, on evaporation at ordinary temp., over sulphuric acid.[141] Nickel sulphate under similar conditions furnishes green crystals of **hexahydrated nickel chlorate,** $Ni(ClO_3)_2.6H_2O$; the two salts are very similar in general characters; and they appear to be closely related with the hexaquo-salts of magnesium and zinc chlorates; all four salts also form tetraquo-salts. When the cobalt salt is warmed slightly—about 18·5°—it gives **tetrahydrated cobalt chlorate,** $Co(ClO_3)_2.4H_2O$, and when dried over phosphorous pentoxide, **dihydrated cobalt chlorate,** $Co(ClO_3)_2.2H_2O$. The hexaquo-nickel salt is transformed at about 39° into **tetrahydrated nickel chlorate,** $Ni(ClO_3)_2.4H_2O$. The nickel salt is too unstable to enable the existence of the dihydrated chlorate to be established. Hexahydrated cobalt and nickel chlorates melt respectively at 61° and 80°, and lose water, decomposing into chlorine, oxygen, and the metal sesquioxide; the reaction is very rapid at 100°. The compounds are not very stable, and their stability is less the smaller the proportion of combined water. Even in aq. soln., at ordinary temp., the salts slowly decompose. According to A. Meusser, the solubility of cobalt chlorate, expressed in percentage amounts of the anhydrous salt, is:

	−21°	0	10·5	18°	21°	35°	61
Per cent. $Co(ClO_3)_2$.	53·30	57·45	61·83	64·19	64·39	67·09	76·12
Solid phase . .	$Co(ClO_3)_2.6H_2O$			$Co(ClO_3)_2.4H_2O$			

With ice as the solid phase, the solubility at −22° is 37·40; and at −12°, 29·97. The corresponding data for nickel chlorate are:

	−18°	0°	18°	40°	48·5°	55°	79·5°
Per cent. $Ni(ClO_3)_2$.	49·55	52·66	56·74	64·47	67·60	68·78	75·50
Solid phase . .	$Ni(ClO_3)_2.6H_2O$				$Ni(ClO_3)_2.4H_2O$		

With ice as the solid phase, the solubility at −13·5° is 31·85, and at −9°, 26·62. F. Ephraim and A. Jahnsen prepared **tetrammino-cobalt chlorate,** $Co(ClO_3)_2.4NH_3$, but found it to be too readily decomposed to determine the vap. press. curve. If a soln. of luteo-cobalt chloride, $Co(NH_3)_6Cl_3$, be treated with sodium chlorate, a fine crystalline powder is precipitated, which, when recrystallized from water, gives needle-like crystals of cobaltihexammino-chlorate, $[Co(NH_3)_6](ClO_3)_3.H_2O$, very soluble in water and dil. alcohol. It detonates by percussion. If a soln. of this salt be mixed with luteo cobalt sulphate, $[Co(NH_3)_6]_2(SO_4)_3.5H_2O$, octahedral crystals of cobalt hexammino-sulphato-chlorate, $[Co(NH_3)_6](SO_4)ClO_3$, are formed, very sparingly soluble in water. F. Ephraim and A. Jahnsen prepared blue needle-like crystals of **hexammino-nickel chlorate,** $Ni(ClO_3)_2.6NH_3$, of sp. gr. 1·52, and melting at 180°. The dissociation press. is 50 mm. at 120°; 75 mm. at 140·5°; and 140 mm. at 15°. It decomposes explosively in an open tube at 201°, and in a closed tube at 240°. The heat of formation is 17·5 Cals. The salt prepared by alcohol precipitation is poorer in ammonia, and approximates to **nickel aquo-pentammino-chlorate,** $Ni(ClO_3)_2.H_2O.5NH_3$.

C. F. Rammelsberg[142] prepared red octahedral (cubic) crystals of **hexahydrated cobalt bromate,** $Co(BrO_3)_2.6H_2O$, with a solubility of 45·5 grms. in 100 grms. of water at ordinary temp. Unstable green crystals of **hexahydrated nickel bromate,** $Ni(BrO_3)_2.6H_2O$, are formed in a similar manner. The crystalline form of these two salts resemble those of the corresponding salt of zinc and magnesium. Alcohol

precipitates from the soln. of the nickel salt in aqua ammonia, a bluish-green crystalline powder of **diammino nickel bromate,** $Ni(BrO_3)_2.2NH_3$. C. F. Rammelsberg prepared what he regarded as **nickel diammino-bromate,** $Ni(BrO_3)_2.2NH_3$ by adding alcohol to an ammoniacal soln. of nickel bromate. F. Ephraim and A. Jahnsen prepared **nickel hexammino-bromate,** $Ni(BrO_3)_2.6NH_3$, of sp. gr. 1·99 and mol. vol. 209·3. Its heat of formation is 17·1 Cals. It detonates in an open tube at 195°–196°, and in a closed tube at 190°–193°; it also detonates by percussion.

Cobalt iodate was first prepared in 1838 by C. F. Rammelsberg,[143] as a violet-coloured salt with 1 or 1½ molecules of water of crystallization, and which had a solubility of 0·68 in 100 parts of cold and 1·11 in 100 parts of boiling water. In 1877, F. W. Clarke reported hydrates with two and with six molecules of water of crystallization. The latter was obtained in long red crystals by the slow evaporation of a soln. of cobalt carbonate in iodic acid. It would be remarkable, said he, if this salt did not exist, because the normal chlorates, bromates, nitrates, sulphates, etc. *crystallize with six molecules of water of crystallization. Against this,* the iodates usually do crystallize with less water of crystallization than the chlorates or nitrates, and A. Meusser, repeating F. W. Clarke's preparation, obtained tetrahydrated cobalt iodate, and not the hexahydrated salt. Yet, again, in 1890, A. Ditte reported hydrates with 2, 3, 4, and 5 molecules of water of crystallization, but A. Meusser failed to confirm A. Ditte's hydrates with three and five molecules of water of crystallization; C. F. Rammelsberg's hydrated salt was probably a mixture of the anhydrous salt and the hydrate with two molecules of water of crystallization. Hence, there remain but two hydrates whose existence have been recognized as indubitable. A. Ditte first prepared bluish-violet needle-like crystals of anhydrous **cobalt iodate,** $Co(IO_3)_2$; by evaporating at about 90° a mixed soln. of cobalt nitrate and potassium chlorate in the presence of an excess of nitric acid; and A. Meusser made it by heating for 2 or 3 hrs., at 120° in a sealed tube a mixture of the same two salts. If a highly conc. soln. of the same two salts be boiled a flocculent pale rose-coloured hydrated precipitate is formed which soon passes into bluish-violet anhydrous cobalt iodate. The same salt is formed by the desiccation of the hydrated salts at 165°; and at 200°, it decomposes into iodine, oxygen, and cobalt oxide. The percentage solubility of the anhydrous salt—per cent. of $Co(IO_3)_2$—is 1·03 at 18°; 0·85 at 50°; 0·75 at 75°; and 0·69 at 100°. Pale lilac-coloured crystals of **dihydrated cobalt iodate,** $Co(IO_3)_2.2H_2O$, are made by evaporating at about 30° equimolecular proportions of cobalt nitrate and alkali iodate in ten times their weight of water; the tetrahydrated salt also passes into the dihydrated salt at about 70° (A. Ditte); the transition is rapid at this temp., and much slower at lower temp., 30°. The solubility of the dihydrated cobalt iodate—per cent. $Co(IO_3)_2$—is 0·32 at 0°; 0·45 at 18°; 0·52 at 30°; 0·67 at 50°; 0·84 at 75°; and 1·02 at 100°. Red hexagonal plates of **tetrahydrated cobalt iodate,** $Co(IO_3)_2.4H_2O$, were made by A. Ditte by mixing conc. boiling soln. of cobalt nitrate and sodium iodate, and cooling, and by dissolving freshly precipitated cobalt carbonate in hydriodic acid. A. Meusser also obtained these crystals by mixing 5 per cent. soln. of hydriodic acid and cobalt nitrate in eq. proportions between 0° and 20°. The solubility of tetrahydrated cobalt iodate—per cent. of anhydrous salt—is 0·54 at 0°; 0·83 at 18°; 1·03 at 30°; 1·46 at 50°; 1·86 at 60°; and 2·17 at 65°. The solubilities of these three forms in water are illustrated in Fig. 23. In all cases, therefore, cobalt iodate is a sparingly soluble salt. The determination of the solubilities at temp. outside the range of stability of particular hydrated salts is possible only when the speed of transition from one form to another is sufficiently slow to allow a sat. soln. to be formed—*e.g.* it was not found possible to prepare a sat. soln. of the anhydrous salt below 0°. The great difference in the solubilities of these different forms does not exclude the possibility of the existence of intermediate hydrates.

C. F. Rammelsberg also prepared what he thought to be a monohydrated nickel iodate analogous with his cobalt salt; F. W. Clarke similarly reported a hexahydrated nickel iodate, and A. Ditte, green prismatic crystals of trihydrated nickel iodate.

A. Meusser was unable to prepare any of these salts. He found that Rammelsberg's salt was probably a mixture of the dihydrated nickel iodate and the anhydrous salt; and Ditte's salt a mixture of possibly tetrahydrated nickel iodate, with a lower hydrated form. Small yellow needle-like crystals of the anhydrous **nickel iodate,** $Ni(IO_3)_2$, are made, as in the case of the corresponding cobalt salt, by heating the metal nitrate with iodic acid with 40 per cent. nitric acid at about 100°. A. Jahnsen gives 5·07 for the sp. gr., and 80·6 for the mol. vol. of anhydrous nickel iodate. The anhydrous salt passes into the hydrated forms extremely slowly, no appreciable hydration being noticed after standing three months in contact with water. Its *solubility, per 100 parts of soln.*, is 1·13 at 30°; 1·07 at 50°; 1·02 at 75°; and 0·988 at 90°. Green hexagonal prismatic crystals of **tetrahydrated nickel iodate,** $Ni(IO_3)_2.4H_2O$, were formed by evaporating a mixture of sodium iodate and nickel nitrate between 0° and 10°. Its solubility, per 100 parts of soln., is 0·73 at 0°; 1·01 at 18°; and 1·41 at 30°. This salt decomposes at temp. approaching 100°. Two distinct forms of the dihydrated salt were prepared by A. Meusser. The first form, **α-dihydrated nickel iodate,** $Ni(IO_3)_2.2H_2O$, is formed when a mixture of nickel nitrate and iodic acid is allowed to stand for some days between 25° and 50°; the voluminous precipitate first assumes a crystalline structure which appears as a green crust on the walls of the vessel. The solubility, per 100 parts of soln., 0·53 of $Ni(IO_3)_2$ at 0°; 0·68 at 18°; 0·86 at 30°; and 0·78 at 50°. The second form,

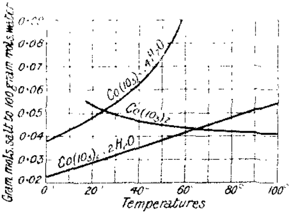


FIG. 23.—Solubility Curves of the Cobalt Iodates.

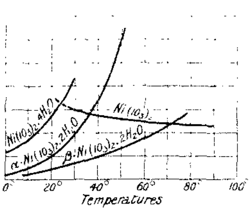


FIG. 24.—Solubility Curves of the Nickel Iodates.

β-dihydrated nickel, $Ni(IO_3)_2.2H_2O$, is less soluble than the α-variety, and is formed in green prismatic crystals, when the α-variety is allowed to stand for half an hour in contact with water at 50°. It is also obtained directly by keeping the soln. required for the α-variety between 50° and 70°. The solubility, per 100 grms. of soln., is 0·52 grm. of $Ni(IO_3)_2$ at 8°; 0·55 at 18°; 0·81 at 50°; 1·03 at 75°; and 1·12 at 80°. The solubility and crystalline form sharply distinguish the two varieties. The solubility curves of the different forms of nickel iodate are illustrated in Fig. 24. The solubilities of the iodates of cobalt and nickel is greater the higher the degree of hydration of the salt, and the hydrates have a higher solubility than the anhydrous salt, and the anhydrous salt has a higher solubility cold than it has hot.

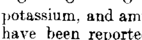
C. F. Rammelsberg prepared what appears to be **nickel tetrammino-iodate,** $Ni(IO_3)_2.4NH_3$, as a pale blue crystalline powder, by the addition of alcohol to a soln. of nickel iodate in ammonia; he also prepared a similar **cobalt tetrammino-iodate,** $Co(IO_3)_2.4NH_3$. F. Ephraim and A. Jahnsen prepared **trihydrated nickel pentammino-iodate,** $Ni(IO_3)_2.5NH_3.3H_2O$, in reddish-violet columnar crystals, and from it they obtained pale violet crystals of **nickel pentammino-iodate,** $Ni(IO_3)_2.5NH_3$, of sp. gr. 2·97, and with a dissociation press. of 179 mm. at 53°; 365 mm. at 65°; 670 at 77°; and 905 mm. at 79°. The ammino-iodates do not explode when heated in open tubes, but they do so in closed tubes between 210° and 219°. The mol. vol. of the pentammino-salt is 166·2, and the mol. vol. of each NH_3 is 17·1. The heat of formation of the pentammine is 12·5 Cals.

F. Ephraim showed that the vol. of the central metal of A. Werner's scheme for *representing the constitution of the ammino-compounds*, is related with the stability of the compound; and A. Jahnsen gives in illustration the hexammino-chlorates $M(ClO_3)_2.6NH_3$:

M	Ni	Cu	Zn	Cd
v, At. vol. M. . .	6·59	7·1	9·1	12·9
T, Diss. temp. at 760°	477°	310°	283·5°	394·5°
$(vT)^{\frac{1}{3}}$ . . .	14·61	13·02	13·73	17·22

The value of $(vT)^{\frac{1}{3}}$ for the cadmium salt is abnormal.

Complex salts and acids.—A series of **sulphato-iodic acids** has been prepared When a soln. of iodine in sulphuric acid is heated to 250° or 260° for a long time, the liquid becomes black, and deposits yellow crystals; the same crystals are formed by dissolving iodine in a soln. of iodic acid in sulphuric acid.[144] These crystals with the composition $H_2O.2SO_3.2I_2O_5$ are decomposed by water. M. M. P. Muir prepared the sulphato-iodic anhydride, $I_2O_5.2SO_3$, by heating a mixture of iodine pentoxide and sulphur trioxide in a sealed tube at 100°; R. Weber represents the composition of the crystals by $I_2O_5.3SO_3$ The supposed $5I_2O_5.SO_3$ of H. Kämmerer is probably not a chemical individual. Several have noted the formation of a compound, $KHSO_4.KIO_3$, *that is*, $2K_2O.I_2O_5.2SO_3.2H_2O$, *and the corresponding ammonium salt*.

R. F. Weinland and G. Barttlingck[145] have reported potassium, ammonium, and rubidium salts of **selenatomonoiodic acid**, $2R_2O.I_2O_5.2SeO_3.H_2O$; and of **selenatotriiodic acid**, $2R_2O.3I_2O_5.2SeO_3.5H_2O$; the former were prepared from eq. quantities of iodic and selenic acids; and the latter from iodic acid and a large excess of selenic acid. R. F. Weinland and H. Prause have prepared potassium, ammonium, and rubidium salts of **monotellurato-monoiodic acid**, $R_2O.I_2O_5.TeO_3.2H_2O$; and of **di-telluratomono-iodic acid**, $R_2O.I_2O_3.2TeO_3.6H_2O$. When sodium iodate and molybdic acid are boiled with water, slender crystals separate from the soln., the crystals are slightly soluble in water, and soluble in nitric acid; their composition corresponds with $I_2O_5.2MoO_3.Na_2O.H_2O$; when the barium salt, obtained similarly, is decomposed with sulphuric acid, a soln. of **molybdato-iodic acid**, $I_2O_5.2MoO_3.2H_2O$, is formed, and the solid acid can be obtained by evaporation in vacuo. A long series of acid salts, $(I_2O_5.2MoO_3)_m.nM_2O.pH_2O$, have been reported by P. Chrétien and C. W. Blomstrand[146]—here m ranges from 1 to 5; n from 1 to 4; and M represents eq. atoms of potassium, sodium, ammonium, lithium, barium, strontium, calcium, magnesium, zinc, cadmium, cobalt, nickel, copper, silver, and manganese. A still more complex silver salt, $4I_2O_5.3MoO_3.4Ag_2O$, and a uranium salt, $4I_2O_5.3MoO_3.2(UO)_2O.3H_2O$, have been made. P. Chrétien and C. W. Blomstrand also made potassium and ammonium salts of **tungstenatoiodic acids**: $M_2O.I_2O_5.2WO_3.nH_2O$, and $2M_2O.I_2O_5.2WO_3.nH_2O$. A. Berg made alkali, ammonium, magnesium, cobalt, nickel, copper, and silver salts of **chromatoiodic acid**,  and A. Ditte, salts of **vanadatoiodic acid.** Lithium, sodium, potassium, and ammonium salts of **phosphatoiodic acid**, $nM_2O.P_2O_5.18I_2O_5.mH_2O$, have been reported by G. S. Sérullas,[147] C. W. Blomstrand, and P. Chrétien. R. F. Weinland and co-workers have reported potassium, ammonium, sodium, rubidium, cæsium, pyridine, and benzene salts of **di- and tri- fluor-iodic acid** in which one or more oxygen atoms are replaced by fluorine—*e.g.* the difluoiodate, MIO_2F_2; the trifluoiodate, $IOF_3.5H_2O$, or $IF_3(OH)_2.4H_2O$; and the tetrafluoiodate, $MIO_2F_2.HIO_2F_2.2H_2O$.

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§ 14. Perchloric Acid and the Perchlorates

In a paper: *Von den Verbindungen des Chlorine mit dem Sauerstoff* (1816), F. von Stadion [1] described the action of sulphuric acid on potassium chlorate; he

found that gaseous chlorine dioxide was given off, and the potassium salt of a new acid, more oxygenated than chloric acid, remained as a solid residue. He said:

> A certain quantity of dried and powdered potassium chlorate is mixed in small quantities at a time, with twice its weight of conc. sulphuric acid, and allowed to stand for 24 hrs. with frequent agitation. The mixture is then warmed on a water-bath until it has lost its colour and smell. Water is then added to dil. the free sulphuric acid; the solid is separated by filtration, and washed with small quantities of cold water until it has lost its acid taste. The residue on the filter is a salt whose weight is equal to 0·28th of that of the chlorate employed. . . . I call the new salt *oxygenated potassium chlorate*. When this salt is mixed with its own weight of sulphuric acid, dil. with one-third its weight of water, and warmed, the salt is decomposed. At a temp. of about 140°, water vapour at first passes off, and afterwards white vapours which condense in a receiver as a liquid acid. When no more vapour is given off, I raised the temp., the white vapours again appeared, but as they were accompanied by chlorine, I suspended the operation. I call the liquid acid in the receiver *oxygenated chloric acid*; it contains a little hydrochloric and sulphuric acids. The latter can be separated by the careful addition of baryta water, and the former by means of silver oxide.

The monohydrate of perchloric acid was prepared by G. S. Sérullas[2] in 1831, and mistaken for anhydrous perchloric acid until H. E. Roscoe prepared the latter in 1862. A. Michael and W. T. Conn isolated the anhydride of perchloric acid—chlorine heptoxide, Cl_2O_7—in 1900.

It will be observed that potassium hypochlorite is the first product of the action of chlorine upon potassium hydroxide, and the hypochlorite is successively converted into the chlorate or perchlorate, before it is finally all transformed into the chloride. The hypochlorite, chlorate, and perchlorate thus represent intermediate stages in the reaction: $4KOH+2Cl_2=4KCl+2H_2O+O_2$. G. D. Liveing[3] compared such reactions with a ball rolling slowly down steps, Fig. 25. The ball may rest on one of the steps, or, if its velocity be great enough, it may roll down to the ground; so, the mixture of chlorine and potassium hydroxide starts with an amount of available energy eq. to 445 Cals.; if the temp. be 0°, when the reaction has done work eq. to 305 Cals., it will stop with the formation of hypochlorite, although it can still do work eq. to 145 Cals. of thermal energy; if the temp. be 100° the system will cease to react when all the hypochlorite has been transformed into chlorate, although the system can now do work eq. to 53 Cals. of thermal energy. The principle here developed is sometimes called W. Ostwald's *Gesetz der Umwaldungstufen*—**the law of successive reactions**—if a chemical process takes place with the formation of a series of intermediate compounds, that compound which involves the smallest expenditure of available energy will be formed first, and so on. According to H. W. B. Roozeboom, observations show merely that W. Ostwald's law of successive reactions is sometimes applicable.

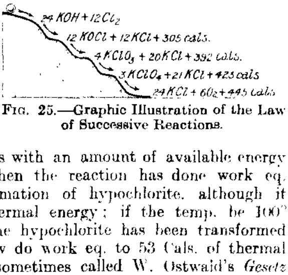


FIG. 25.—Graphic Illustration of the Law of Successive Reactions.

The effect of manganese dioxide on decomposing potassium chlorate is to mask or abbreviate the intermediate stages which occur before the system has assumed the final most stable condition. Similarly, the different stages in the reaction between chlorine and potassium hydroxide can be suppressed by passing the chlorine into a warm solution of potassium hydroxide admixed with a little cobalt salt. Oxygen is then given off and potassium chloride is formed immediately without any signs of the hypochlorite, etc. There are also several reactions in which the catalytic agent accelerates a side reaction at the expense of the main reaction; and others in which the products of the reaction are quite different with and without the catalytic agent.

The preparation of perchloric acid and the perchlorates.—Perchlorates are produced in a chemical way by the breaking up of a chlorate, and by the direct

oxidation of chlorates. T. Fairley[4] reported the formation of perchloric acid and of its salts by the passage of ozonized air into a soln. of hypochlorous acid or of a hypochlorite: $HOCl+O_3=HClO_4$. Hydrogen peroxide oxidizes chlorine to hypochlorous acid: $Cl_2+H_2O_2=2HOCl$. C. W. Bennett and E. L. Mack also found that chlorates are oxidized to perchlorates by exposure to oxygen activated by ultra-violet light; by persulphuric acid and by ozone in acid soln. J. G. Fowler and J. Grant showed that the chlorates are oxidized to perchlorates when heated with silver oxide. The genesis of the perchlorates can be traced back to the fundamental reaction between chlorine and cold alkaline lye: $Cl_2+2KOH=KOCl+KCl+H_2O$; for the hypochlorite when warmed changes into chloride and chlorate: $3KOCl=KClO_3+2KCl$; and the chlorate oxidizes itself, so to speak, when heated, $4KClO_3=3KClO_4+KCl$. F. von Stadion and N. A. E. Millon[5] found that an aq. soln. of chlorine dioxide in light also decomposes into chloric and perchloric acids, but not in darkness; and A. Popper showed that the perchloric acid is formed at the expense of the chloric acid. G. S. Sérullas also noted some formation of perchloric acid when chloric acid is distilled; and N. A. E. Millon, when chloric acid is allowed to stand some time beside conc. sulphuric acid. In general, the perchlorates are formed when the chlorates are decomposed by electrolysis, by sulphuric acid (F. von Stadion, 1816), by nitric acid (F. Penny, 1841), or by heat (G. S. Sérullas, 1830). A soln. of chloric acid is unstable when its concentration exceeds a certain value; and W. Oechsli[6] has shown reasons for assuming that it breaks up into perchloric and chlorous acids: $2HClO_3=HClO_4+HClO_2$; the chlorous acid, $HClO_2$, reacts with the chloric acid in accord with the reversible reaction, $HClO_3+HClO_2\rightleftharpoons H_2O+2ClO_2$. There is a formal analogy between these reactions and the way hypochlorous acid breaks up first into chloric and hydrochloric acids: $3HOCl=HClO_3+2HCl$, followed by a reversible reaction between the hydrochloric and hypochlorous acids: $HOCl+HCl\rightleftharpoons H_2O+Cl_2$.

The formation of alkali perchlorates by heating the alkali chlorates up to the temp. at which the molten liquid becomes more viscid, $4KClO_3=3KClO_4+KCl$, or $2KClO_3=KCl+O_2$, and afterwards separating the chloride and perchlorate by fractional crystallization, has been discussed—*vide* oxygen—and D. A. Kreider[7] recommended heating sodium chlorate until it had decomposed into the perchlorate; and evaporating the residue with conc. hydrochloric acid to dryness. The perchlorate was extracted with conc. hydrochloric acid in which the sodium chloride is but sparingly soluble. The liquid is then treated with 97 per cent. alcohol in which sodium perchlorate is alone soluble. The clear liquid is conc., and the sodium perchlorate separates in a crystalline condition.

Aq. soln. of perchloric acid have been made by the distillation of a mixture of potassium chlorate with, say, four times its weight of conc. sulphuric acid;[8] by warming an aq. soln. of potassium perchlorate (1 : 7) with a small excess of hydrofluosilicic acid, H_2SiF_6, for an hour, and filtering the cooled liquid. The addition of a little barium perchlorate or chloride to the dil. soln. will remove the slight excess of hydrofluosilicic acid. The clear liquid can then be evaporated. O. Henry[9] also made an aq. soln. of the acid by the decomposition of barium perchlorate with sulphuric acid. D. A. Kreider[10] prepared an aq. soln. of perchloric acid by treating sodium perchlorate with an excess of conc. hydrochloric acid in which sodium chloride is but sparingly soluble: $NaClO_4+HCl=HClO_4+NaCl$. The filtered liquid, after heating to 135°, does not contain enough hydrochloric acid to give an opalescence with silver nitrate. F. C. Mathers' directions are:

Dry sodium perchlorate, 20 grms., is treated with 25 to 30 c.c. of conc. hydrochloric acid. The sparingly soluble sodium chloride is filtered through an asbestos filter, and washed with ten 1 c.c. portions of conc. hydrochloric acid. The filtrate contains the aq. perchloric acid and the excess of hydrochloric acid, together with the small amounts of the sodium salts of these acids which are soluble in conc. hydrochloric acid. The mixed filtrate and washings, at 135°, are evaporated on a hot plate to volatilize the hydrochloric acid; the soln. of perchloric acid which boils at 205° remains behind. The yield is about 95 per cent. of the theoretical. About one per cent. of sodium perchlorate is lost in the sodium

chloride residues, the other four per cent. is present in the perchloric acid as sodium perchlorate. The process does not work so well with the potassium or barium salt.

F. C. Mathers, and A. W. Kenney prepared perchloric acid by distilling a mixture of potassium perchlorate and sulphuric acid in a current of steam. H. H. Willard oxidized ammonium perchlorate with an excess of a mixture of nitric and hydrochloric acids. As a result, a mixture of perchloric, nitric, and hydrochloric acids is formed. The latter are expelled by heating the mixture on a hot plate until white fumes of perchloric acid begin to appear. No unoxidized ammonia should be present in the soln. *An acid of a composition approximately* $HClO_4+2H_2O$, *boiling at 203°*, remains.

F. von Stadion's preparation (1816) was really an aq. soln. containing about 70 per cent. of $HClO_4$; G. S. Sérullas' preparation (1831) was the crystalline monohydrate, $HClO_4.H_2O$, which was mistaken for the pure acid until H. E. Roscoe [11] demonstrated that it contained water, and by fractional distillation obtained from it a small quantity of what he called pure perchloric acid. H. E. Roscoe's directions are:

Pure dry potassium perchlorate is distilled in a small retort with four times its weight of conc. sulphuric which has been previously boiled. Dense white fumes begin to be evolved at about 110°, and a colourless yellow liquid, consisting of perchloric acid, distils over. The product in the receiver is generally contaminated with a little sulphuric acid carried over mechanically. If the distillation be continued, the liquid in the receiver gradually changes into a white crystalline mass with the composition $HClO_4.H_2O$. This hydrate is formed from the water which is produced by the decomposition of a portion of the perchloric acid into a chlorine oxide, oxygen, and water. If the crystalline hydrate is again heated, it decomposes into the pure acid which distils over, and into an aq. soln. of the acid which boils at 203°, and therefore remains behind in the retort.

An aq. soln. of perchloric acid contains about 70 per cent. of $HClO_4$—approximating to the dihydrate—when it has been evaporated on a hot plate until dense white fumes appear. If this acid be distilled at ordinary press., when it boils at 203°, about 10 per cent. is decomposed. Perchloric acid can be heated without decomposition under reduced press. much above the temp. at which it begins *to decompose under ordinary atm. press. Perchloric acid boils at 19° under a press.* of 11 mm., and between 135° and 145° when the press. is between 50 and 70 mm. Consequently, if a mixture of perchloric and sulphuric acids be fractionally distilled under reduced press., *the perchloric acid volatilizes at a lower temp.*, and its decomposition is largely avoided. A. Vorländer and R. von Schilling [12] distilled the acid between 45 and 50 mm.: A. Michael and W. T. Conn between 10 and 20 mm.; T. W. Richards and H. H. Willard between 150 and 200 mm., and between 15 and 20 mm.

D. Vörländer and R. von Schilling heated 50 grms. of powdered potassium chlorate with between 150 and 175 grms. of conc. sulphuric acid (96–97·5 per cent. H_2SO_4), in a 300 c.c fractionating flask, immersed in an oil-bath, with the level of the oil below the level of the liquid in the flask. The contents of the flask are distilled under a press. of 50–70 mm., at 135° to 145°. An air condenser 75 cm. long leads to a glass condenser immersed in a freezing mixture of ice and salt. In about 1½ to 2 hrs. 22·24 grms. of crude anhydrous perchloric acid are obtained. The gases from the condenser containing the oxides of chlorine are passed through a tube containing soda lime; the glass joints are luted with a mixture of asbestos and water glass.

The crude perchloric acid so prepared is coloured yellow owing to the presence of chlorine dioxide, and contains about one per cent. of sulphuric acid and traces of hydrochloric acid. D. Vorländer and R. von Schilling rectified the acid by aspirating air through a capillary tube dipping in the acid contained in a fractionating flask heated on a water-bath until the acid lost its yellow tinge. The acid is then distilled under reduced press.—say at 45°–65° under a press. of 50–70 mm. Sulphuric acid with some monohydrated perchloric acid remains in the flask, and 18–21 grms. of colourless acid is obtained. T. W. Richards and H. H. Willard found that after three distillations under a press. of about 15–20 mm., 90 per cent. of the last distillate

was quite free from sulphuric acid, and 9 per cent. showed so little that after evaporating off all but 1 c.c., nothing more than a faint opalescence was obtained with barium chloride. A trace of phosphoric acid is usually present in the crude acid, but the second distillate is free from this impurity.

Electrolytic processes for the perchlorates.—F. von Stadion found that if an aq. soln. of chlorine dioxide be "included in Volta's circuit," at first very little gas is developed, but after some hours, oxygen and chlorine appear at the anode, and hydrogen at the cathode. The volume of hydrogen so obtained is nearly twice that of the oxygen. After some time the soln. is decolorized, and transformed into perchloric acid. In 1857, A. Riche[13] prepared perchloric acid by the electrolysis of hydrochloric acid, or of an aq. soln. of chlorine; and ten years earlier, H. Kolbe prepared potassium perchlorate by the electrolysis of an aq. soln. of potassium chloride—acidified with sulphuric acid and of potassium trichloromethyl-sulphonate. H. Kolbe (1846), a pioneer in the electrolytic preparation of compounds, specially noted that the formation of perchloric acid is always preceded by that of chloric acid, and stated:

> The production of perchloric acid in an acid soln. is certainly a fact worthy of attention, for, according to all the observation hitherto made, combination between chlorine and oxygen could be effected only in the presence of a free alkaline base ready to unite with the newly formed acid.

W. Oechsli[14] put forward the hypothesis that the chlorates are not oxidized to perchlorates by anodic oxygen as represented by the equation: $ClO_3'+2OH'=ClO_4'+H_2O$, but the oxidation is rather a secondary reaction attending the anodic discharge of the chlorate ion: $2ClO_3+H_2O=2HClO_3+O$. The free chloric acid is probably present in a very highly conc. condition about the anode, and, since in this condition it is known to be unstable, it spontaneously decomposes into perchloric and chlorous acids: $2HClO_3=HClO_4+HClO_2$. The free chlorous acid thus formed cannot remain in the soln., for, in contact with the chloric acid which is present, it would immediately evolve chlorine dioxide: $HClO_3+HClO_2=H_2O+2ClO_2$; but no such evolution of chlorine dioxide has been observed, and it is hence assumed that the chlorous acid is instantaneously oxidized to chloric acid by the oxygen liberated from the decomposition of water by discharged ClO_3-ions: $2ClO_3+H_2O=2HClO_3+O$, which reacts with the chlorous acid: $HClO_2+O=HClO_3$. The end products of the secondary reaction following the discharge of the chlorate ions are therefore: $2ClO_3+H_2O=HClO_4+HClO_3$.

To this hypothesis C. W. Bennett and E. L. Mack reply that there is no direct evidence that chloric acid, when sufficiently conc., decomposes with the formation of perchloric and chlorous acids. The visible products of the decomposition are known to be perchloric acid, chlorine dioxide, chlorine, and oxygen, but the possible formation of chlorous acid has not been demonstrated satisfactorily. They also assume that the chlorate ion is directly oxidized at the anode, and show that the general phenomena observed during the perchlorate formation are most easily and satisfactorily explained from this view-point. The action of the current on electrolytes containing oxygen or hydroxyl ions is to liberate active or atomic oxygen[15] which, unless depolarized by some substance present in the soln., will be converted into ordinary oxygen gas: $2O=O_2$. The rate of this reaction, and consequently also the concentration of the active atomic oxygen, is dependent on (i) the nature of the anode; (ii) the current density; (iii) the temp.; (iv) the nature of the soln.; and (v) the elapsed time of electrolysis. In order to oxidize a substance—*e.g.* a chlorate ion—present in the electrolyte, C. W. Bennett and E. L. Mack further show that the potential of the anode should not rise to that point necessary to bring about the liberation of gaseous oxygen, but only to that point necessary to produce a concentration of active oxygen sufficient to oxidize the chlorate ion, for E. P. Schoch[16] has shown that in a $\frac{1}{2}N$-soln. of potassium chlorate with an iron anode, the formation of perchlorate begins when the anode potential is 0·023 volt, a number well

below the discharge potential of chlorate ions. With the same system, the evolution of oxygen did not commence until the anode potential had reached 1·5 volts. Hence it is inferred that the formation of perchlorate is not determined by the discharge of chlorate ions, as W. Oechsli supposes, even though in practice the potential of the anode during the electrolysis of a chlorate soln. is above that necessary for the discharge of the chlorate ions. The direct oxidation of chlorate *ions*, ClO_3', *in general, requires a lower potential than the discharge of these ions*, and will therefore take place. Those factors which unfavourably affect the oxidation process are those which lower the concentration of active oxygen at the anode. If the unfavourable factors predominate, there will be a greater tendency for oxygen gas to be evolved and a drop in the current efficiency with respect to the formation of perchlorate, in confirmation of the hypothesis that the electrochemical formation of perchlorates is a direct oxidation of the chlorates by active atomic oxygen on the anode.

C. W. Bennett and E. L. Mack have shown that the chlorates are oxidized to perchlorates by persulphates and ozone, in acid soln.: $HClO_3+O=HClO_4$. The *self-oxidation of the chlorates to perchlorates*: $4KClO_3=3KClO_4+KCl$, when heated to moderate temp., and the direct oxidation of chlorates by silver oxide observed by J. G. Fowler and J. Grant,[17] is evidence of the oxidation of chlorates to perchlorates.

F. Winteler [18] has studied the conditions favourable for the production of perchlorates, and found that if the concentration of the chloride exceeds 10 per cent., very little perchlorate will be formed in warm soln. The anode temp. should be kept low by artificial cooling, since the yield falls when the temp. is raised; and it is preferable to have a high concentration of chlorate. In the electrolysis of alkali chloride soln., no perchlorate is formed until nearly all the chloride has been converted to chlorate. *The yield is reduced in alkaline soln. probably owing to the* smaller number of chlorate ions and the increasing number of hydroxyl ions liberated as the alkalinity is increased—hydroxyl ions are more easily discharged than chlorate ions. Increasing the current density counteracts the effect of increasing alkalinity.

According to J. G. Williams, the production of perchlorate is improved if a higher temp. be maintained and acid frequently added; during electrolysis, for each temp., there is an equilibrium between the decomposition of chloric acid at the anode with the formation of chlorides. In present-day practice, the temp. of the electrolysis is initially about 30°, and the current density about 45–50 amps. per sq. dm. The soln. used has about 600–700 grms. per litre $NaClO_3$. As the chlorate content falls below about 100 grms. $NaClO_3$ per litre, the resistance of the series of baths increases considerably, and at 50 grms. per litre, the current density is about 30 amps. per sq. dm. and the liquor temp. about 45°–50°. Ozone is not given off in appreciable quantities until the chlorate concentration is below 10 grms. per litre; as the chlorate content gets below 5 grms. per litre, the smell of the ozone is almost overpowering, and, if breathed much, produces pains and continuous coughing. The liquor charged should certainly not be alkaline to any appreciable degree, but no advantage is served by acidifying the liquor. Under normal conditions of electrolysis, the average efficiency is 85 per cent. or more.

M. Couleru recommends the use of a conc. soln. of sodium chromate for the successful production of perchlorates. The action is similar to that which is obtained by a little chromate in the electrolyte during the production of chlorates. The sodium perchlorate so produced is very soluble and deliquescent, and it is not usually worked up, but rather converted into the ammonium or potassium salt by the addition of ammonium or potassium chloride. It is advisable to ensure that all the chlorate has been converted into perchlorate before precipitating the perchlorate, otherwise the perchlorate will be contaminated by the chlorate in solid soln. which cannot be removed by washing. A. Angeli recommends electrolyzing

a soln. of calcium chloride, and when all is converted into perchlorate, adding *ammonium chloride* and evaporating to crystallize out the ammonium perchlorate.

The physical properties of perchloric acid.—Anhydrous perchloric acid is a colourless, hygroscopic, volatile, mobile liquid, which fumes in air. When the anhydrous acid comes in contact with the skin, it produces serious and painful wounds. D. Vorländer and R. von Schilling say that the *pure acid decomposes spontaneously in a few weeks even* in the dark; and that the liquid first darkens in colour, and then explodes, while A. Michael and W. T. Conn say that it does not explode. Perchloric acid readily unites with water to form needle-like crystals of the monohydrate, which, *as indicated above, was mistaken* by G. S. Sérullas (1831) for the anhydrous acid. The soln. of the acid in water is much more stable, for it decomposes neither in light nor in darkness if organic matter and reducing agents be excluded. The physical properties of perchloric acid have been investigated by H. E. Roscoe,[19] D. Vorländer and R. von Schilling, and by H. J. van Wijk.

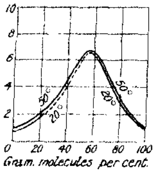


FIG. 26. — Specific Gravity - Concentration Curves of Aqueous Solutions of Perchloric Acid.

The **specific gravity** of perchloric acid, and of aq. soln. of this acid, have been determined by H. J. van Wijk (1905), K. van Emster (1907), H. E. Roscoe (1863),[20] etc. H. J. van Wijk found for the sp. gr. at 20° and 50° referred to water at 4° unity, and corrected for weighings in vacuo, for perchloric acid, $HClO_4$, of the percentage composition :

Per cent. $HClO_4$.	100	94·67	84·81	75·59	60·38	39·73
Sp. gr. 20° . .	1·7676	1·8059	—	1·7386	1·5353	1·2901
Sp. gr. 50° . .	1·7078	1·7531	1·7756	1·7023	1·5007	1·2649

There is therefore *a maximum* in the sp. gr. curve with soln. containing 84·8 per cent. $HClO_4$, or 50 mol. per cent. corresponding with $HClO_4.H_2O$, as illustrated in Fig. 26. K. van Emster's values at 15° also referred to water at 4° unity, and weighings in vacuo are given in Table I. The curve showing the relation between percentage composition and sp. gr. has a slight curvature from 1 to 53 per cent. of $HClO_4$, and from about 53 per cent. $HClO_4$, the curve is a straight line.

TABLE I.—PERCENTAGE COMPOSITION OF SOLUTIONS OF PERCHLORIC ACID OF SPECIFIC GRAVITY BETWEEN 1·00 AND 1·67 AT 15°.

Sp. gr.	0·00	0·01	0·02	0·03	0·04	0·05	0·06	0·07	0·08	0·09
1·0	—	1·90	3·61	5·25	6·88	8·48	10·06	11·58	13·08	14·56
1·1	16·00	17·45	18·88	20·26	21·64	22·64	24·30	25·57	26·82	28·05
1·2	29·26	30·45	31·61	32·74	33·85	34·95	36·03	37·08	38·10	39·10
1·3	40·10	41·08	42·03	42·97	43·89	44·81	45·71	46·61	47·49	48·37
1·4	49·23	50·10	50·91	51·71	52·54	53·31	54·11	54·89	55·56	56·32
1·5	57·06	57·81	58·54	59·28	60·04	60·78	61·52	62·26	63·00	63·74
1·6	64·50	65·26	66·01	66·76	67·76	68·26	69·02	69·77	—	—

The **coefficient of cubical expansion** of anhydrous perchloric acid, $HClO_4$, is 0·0011 between 20° and 50°; and K. von Emster calculates the mean coeff. of expansion α for temp. between θ and θ_2 for soln. with the respective sp. gr. D_1 and D_2, $\alpha=(D_1-D_2)/D_2(\theta_2-\theta_1)$:

Per cent. $HClO_4$ . . .	11·14	35·63	55·63	69·81
α between 15°-50° . . .	0·0004432	0·0006439	0·0007648	0·0007440

There is therefore *a maximum in the coeff. of thermal expansion* with approximately the 55 per cent. acid.

According to H. J. van Wijk, the **boiling point** of anhydrous perchloric acid under a press. of 18 mm. is 16° ; and, according to D. Vorländer and R. von Schilling, at 39° under a press. of 56 mm. The b.p. of the pure acid does not remain constant because there is a partial decomposition of the vapour into the anhydride and water: $2HClO_4=Cl_2O_7+H_2O$, and the liquid has quite a complex composition. There is very little decomposition, however, when the liquid is distilled at a low press., but under ordinary press. decomposition begins at about 70°—chlorine, chlorine dioxide, and oxygen are formed. The distillate has an orange tint owing to the dissolution of chlorine dioxide. Anhydrous perchloric acid explodes towards 90°. Aq. soln. of the acid more conc. than 72·4 per cent. $HClO_4$, or 31·96 mol. per cent. become less conc. by the loss of $HClO_4$ when distilled ; and less conc. soln. become more conc. by the loss of water. The constant boiling acid contains 72·4 per cent. of $HClO_4$, boils at 203°, and distils unchanged in composition. The composition of liquid and vapour for soln. with 72·4 per cent. of $HClO_4$ is illustrated in Table II. The results are plotted in Fig. 27. Mixtures of greater concentration than 72·1 per cent. $HClO_4$ decompose more or less when heated—even the acid boiling at 200° shows some decomposition ; and such acids must be distilled under a reduced press. to reduce

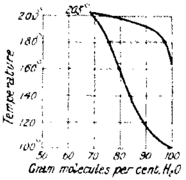


FIG. 27. — Composition of Liquid and Vapour Phases of Solutions of Perchloric Acid of different Boiling Points.

TABLE II.—COMPOSITION OF LIQUID AND VAPOUR PHASES OF SOLUTIONS OF PERCHLORIC ACID OF DIFFERENT BOILING POINTS.

Boiling point.	Per cent. of $HClO_4$.	
	Liquid	Vapour.
203°	72·40	72·40
198·7°	70·06	40·11
181·2°	65·20	6·06
162·3°	61·2	0·90
148·0°	56·65	—
114·8°	38·90	—

decomposition. At 18 mm. press., acids of the following percentage composition boil at the temp. stated :

Per cent. $HClO_4$ . .	100	94·8	92·0	84·8	79·8	70·5
Boils (18 mm.) . .	16·0°	24·8°	35°	70°	92°	107°

The last-named mixture suffers no decomposition when boiled at ordinary temp. Although the constant boiling 72·4 per cent. acid approximates to the dihydrate, $HClO_4.2H_2O$ (73·63 per cent. $HClO_4$), it is not a compound, since, H. E. Roscoe has shown, its composition and b.p. depend on the press. under which the distillation is performed. In this respect, the phenomena are analogous with those presented by other constant boiling acids.

Anhydrous perchloric acid does not freeze when cooled by solid carbon dioxide, but its **freezing point** is −112°. The f.p. curve of mixtures of water and perchloric acid was investigated by H. J. van Wijk, and he found indications of the existence of six hydrates of perchloric acid, containing respectively 1, 2, 2½, 3, and $3\frac{1}{2}H_2O$—the hydrate with $3H_2O$ exists in two different forms. The m.p. curve is shown in Fig. 28. The eutectic between the monohydrate $HClO_4.H_2O$ and the anhydrous acid lies virtually at the m.p. of the latter, −112° ; in consequence the m.p. curve

appears *to rise up to between 49·5° and 50°*, which represents the m.p. of the **monohydrate of perchloric acid,** $HClO_4.H_2O$. During fusion there is a marked expansion. The sp. gr. of the molten hydrate is 1·7756. The **heat of fusion** is 33·7 cals. per gram; when warmed to 110°, it decomposes, and a distillate rich in perchloric acid begins to collect. The monohydrate is formed in long needle-like *crystals by mixing perchloric acid with the requisite* quantity of water; and by

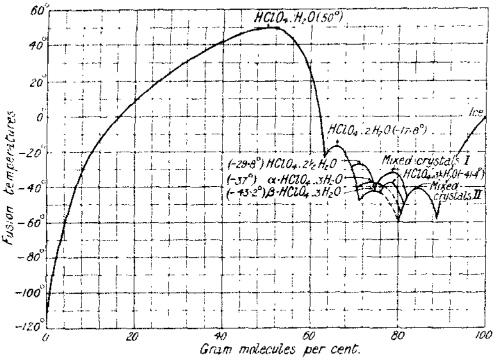


FIG. 28.—Fusion Curve of Mixtures of Perchloric Acid, $HClO_4$, and Water.

the method previously indicated. The fusion curve extends from 0 to 63·5 mol. per cent. of $HClO_4$. *The latter is the eutectic mixture with the eutectic temp.* —23·6°, between the mono- and the **di-hydrate of perchloric acid,** $HClO_4.2H_2O$. The curve then rises to a maximum with the m.p. —17·8°; the curve then falls to a branch curve belonging to the **hemipentahydrate of perchloric acid,** $HClO_4.2\frac{1}{2}H_2O$, which rises from the eutectic —30·3° to the maximum —29·8°. The dihydrate *curve also extends into a metastable system below* —30·3°, *to a branch line at* —46·5°, which rises to a maximum at —43·2°, the m.p. of this metastable **β-trihydrate of perchloric acid,** β-$HClO_4.3H_2O$. The β-trihydrate passes into **α-trihydrate of perchloric acid,** α-$HClO_4.3H_2O$, which melts at —37°. *The fusion curve of the α-trihydrate* cuts the 2½ hydrate curve with 75 mol. per cent. of H_2O, and its region of stability between that point and 76·3 mol. per cent. H_2O. The α-trihydrate fusion curve passes into the fusion curve of **hemi-heptahydrate of perchloric acid,** $HClO_3.3\frac{1}{2}H_2O$, which has a m.p. of 41·4°. The α-trihydrate is metastable in the intervening region, and it as well as the 3½-hydrate readily forms mixed crystals I when the mass has between 75·4 and 82·3 mol. per cent. of water. There is a eutectic at —42·3° with the 2½-hydrate, at —43·8° with the β-trihydrate, and at —37° with the α-trihydrate. Mixed crystals II separate from mixtures with from 80 to 88·7 mol. per cent. of water. These crystals have a eutectic at —60° with the β-trihydrate; at —57·2° with the α-trihydrate, at —52·5° with the 3½-hydrate; at —46° mixed crystals I; and at —57·5° with ice. The latter eutectic corresponds with 88·7 mol. per cent. of water. The **viscosity** of anhydrous perchloric acid is

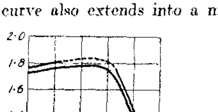


FIG. 29.—Viscosities of Mixtures of Perchloric Acid and Water.

nearly the same as water. H. J. van Wijk's values for 20° and 50° show that the *viscosity rises from that of the anhydrous acid* 1·03 at 50° to 6·87 with soln. containing 80·5 per cent. $HClO_4$; and then falls to 1·13, the value for water at that temp. The results are plotted in Fig. 29.

Thermochemistry of the oxychlorine acids.—Perchloric acid is not so powerful an oxidizing agent as chloric acid, and this in turn is less vigorous than hypochlorous acid. This agrees with the stability of the respective acids, and is in accord with the fact that a greater amount of available energy per atom of available oxygen is associated with hypochlorous acid than with either chloric or perchloric acid. For instance, the thermochemical equations are represented:

$$HOCl_{aq.}=HCl_{aq.}+O+9\cdot3\text{ Cals.}; \text{ or } 9\cdot3 \text{ Cals. per atom of oxygen.}$$
$$HClO_{3aq.}=HCl_{aq.}+3O+15\cdot3\text{ Cals.}; \text{ or } 5\cdot1 \text{ Cals. per atom of oxygen.}$$
$$HClO_{4aq.}=HCl_{aq.}+4O+0\cdot7\text{ Cals.}; \text{ or } 0\cdot2 \text{ Cals. per atom of oxygen.}$$

Since the bleaching effect of these reagents is supposed to depend upon the action of nascent oxygen, it follows that in this case there is no particular need for the assumption that atomic oxygen is more active than molecular oxygen, because the nascent oxygen is associated with a larger amount of available energy, which can do chemical work. The available energy of each acid must be *added to* that which free oxygen could give if it alone were performing the same oxidation; according to the principle of maximum work, the amount of energy degraded during a chemical reaction measures the "tendency of a reaction to take place." Hence, the greater oxidizing properties of these acids must, at least in part, be due to the greater amount of available energy associated with their nascent oxygen during decomposition.

The **heat of formation** of liquid perchloric acid from its elements[21] is $H+Cl+4O=HClO_{4liq.}+19\cdot1$ Cals.; $H+Cl+4O+Aq.=HClO_{4aq.}+39\cdot35$ Cals.; $HClO_{4liq.}=HCl+4O+2\cdot9$ Cals.; $HClO_{4aq.}=HCl_{aq.}+4O+0\cdot7$ Cals. The **heat of solution** is unusually high. When dropped into water, anhydrous perchloric acid combines with the water with a hissing noise, and the evolution of much heat, *viz.* 20·3 Cals., and it is therefore as large as that of phosphorus pentoxide. The heat of soln. of the mono-hydrate is +7·7 Cals., and of the dihydrate +5·3 Cals.; the **heat of neutralization** is $HClO_{4aq.}+NaOH_{aq.}=14\cdot08$ Cals., $HClO_{4aq.}+\frac{1}{2}Ba(OH)_{2aq.}=13\cdot8$ Cals. M. Berthelot gives the heat of dil. of $HClO_3+nH_2O$ with $(600-n)$ mol. of water to be

n . .	0	1·43	2	3·085	5·215	6·28	9·5	96·5
Cals .	20·3	7·37	5·3	1·23	0·31	0·048	−0·237	−0·025

and with $n=196\cdot5$, the heat of dil. is zero; with $HClO_4.H_2O$ crystalline, 7·72 Cals., and with $HClO_4.H_2O$ liquid, 11·7 Cals. W. Ostwald gives the heat of formation *of ClO_4'-ions as −39 Cals. The* **specific heat** *C of soln. of $HClO_4+nH_2O$ between* 15° and 40°, is, according to M. Berthelot, in calories per gram:

n	3·085	5·4	9·59	46·35	590
C	0·501	0·575	0·6705	0·893	0·993

T. W. Richards and A. W. Rowe find 0·9466 for the sp. ht. of a soln. $HClO_4+100H_2O$, and the mol. ht., 1891 cals. B. Käbitz[22] says that perchloric acid gives a continuous **absorption spectrum** from about $29\mu\mu$. According to W. Ostwald,[23] the **molecular conductivity** when a mol. of $HClO_4$ is dissolved in *v* litres of water is,

v	2	8	32	128	256	512	1024	2048	4096
λ	79·1	84·6	88·1	89·2	89·9	89·8	89·8	89·3	87·8

The maximum value is 89·9. This, says W. Ostwald, corresponds with the fact that perchloric acid is one of the strongest of acids, and approaches very near to chloric and nitric acids. The mobility of the ClO_4'-ions at 18° is, according to F. Kohlrausch, about 64; and according to A. E. Baur, at 25°, 67·5.

The properties of perchloric acid.—The aq. soln. of perchloric acid are much

more stable than the anhydrous acid. A soln. of the acid in chloroform becomes yellow when exposed to the air, and forms the monohydrate; a violent explosion occurs if the soln. be poured upon phosphorus pentoxide. The anhydrous acid explodes if the attempt be made to distil it at ordinary press.; at 72°, the acid darkens in colour, at 92° it gives off white vapours and an orange-yellow gas—chlorine dioxide—and a few drops of a distillate as dark in colour as bromine and containing 94·77 per cent. $HClO_4$ are formed; if heated further an explosion occurs. Anhydrous perchloric acid acts as a powerful oxidizing agent on many substances; for example, if a drop be brought in contact with wood charcoal, an explosion almost as violent as that of nitrogen chloride occurs. The anhydrous acid also inflames paper and wood. This acid sometimes explodes when brought in contact with alcohol, at other times it forms ethyl ether; it can be mixed with cold absolute alcohol, when it forms what A. Michael and W. T. Conn regard as ethyl perchlorate; it is insoluble in carbon tetrachloride and benzene; with benzene, it forms a carbonaceous substance. Perchloric acid explodes with well-dried ether; ethyl perchlorate is not formed by alcohol or by ether. Anhydrous perchloric acid with iodine forms deliquescent needles of a substance with the composition HI_7O_3, *i.e.* $HIO_3(I_2)_3$, which when warmed gives off iodine and leaves iodic acid as a residue; the acid inflames with sodium iodide and hydriodic acid. Unlike soln. of chloric acid, an aq. soln. of perchloric acid is not reduced by sulphurous acid, or hydrogen sulphide, nor decomposed by hydrochloric or hydriodic acid, indeed, D. Tommasi, and M. Berthelot have emphasized how very resistant aq. soln. of this acid are to reducing agents generally. Free hydrogen does not reduce perchloric acid, nor does it reduce the fused acid at 300°. It is not reduced by zinc and magnesium, nor by a copper zinc couple. R. Roth says that the 20 per cent. acid attacks most metals in the cold with the evolution of hydrogen—very little reduction of the acid occurs. Metallic silver is dissolved by the acid as silver perchlorate, likewise also behave zinc, iron, nickel, mercury, copper, lead, and tin. Arsenic and antimony give the trioxides which dissolve in hot 60–70 per cent. acid, the former separates out as arsenic trioxide, the latter as antimony perchlorate; by boiling the soln. arsenic and antimony pentoxides are formed. Selenium dissolves in the cold, forming selenious acid, while sulphur and phosphoric acid are attacked only by boiling with the conc. acid. Chromium is not attacked when heated with 60–70 per cent. perchloric acid. Mercuric chloride dissolves in the hot conc. acid, and separates out again as the soln. cools. Ammonia is not oxidized by perchloric acid in the presence of conc. sulphuric acid. H. Toussaint[24] found that nitrous acid is not oxidized even when boiled with perchloric acid; but F. Winteler decomposed soln. of perchloric acid by fuming nitric acid; iodine in the cold is oxidized to iodic acid. B. Sjollema reduced perchloric acid by boiling with neutral ferrous hydroxide, but not with acid ferrous salts; V. Rothmund, by tervalent titanium salts in acid soln., and by the lower oxides of vanadium or molybdenum; but only with extreme slowness by the lower oxides of chromium and tungsten. Perchlorates are also reduced by hyposulphites.

Perchloric anhydride, chlorine heptoxide, Cl_2O_7.—A. Michael and W. T. Conn[25] isolated this oxide, in 1900, by adding anhydrous perchloric acid very slowly to phosphorus pentoxide cooled to −10°, and after the mixture has stood for a day at −10°, distilling the product at 82°. The reaction is symbolized: $2HClO_4+P_2O_5=2HPO_3+Cl_2O_7$. Chlorine heptoxide condenses to a colourless volatile oil which decomposes spontaneously on standing for a few days, when it acquires a greenish-yellow colour. The preparation of chlorine heptoxide is dangerous, for, adc A. Michael and W. T. Conn, "the apparatus may be virtually pulverized by violent explosion, and personal precautions must be taken accordingly." Perchloric anhydride is soluble in benzene, which it slowly attacks; it also reacts with iodine—slowly in darkness, rapidly in light—forming what is supposed to be iodine pentoxide I_2O_5; but it does not react with bromine. Chlorine heptoxide reacts slowly with water, forming perchloric acid; it explodes on contact with flame, and by percussion; it may be poured on to organic matter—paper, wood, etc.—with impunity

for the oil simply volatilizes in air. P. Walden found that chlorine heptoxide dissolves in phosphorus oxychloride, lowering the f.p. of the solvent in accord with the normal molecular state Cl_2O_7.

The properties of the perchlorates.—Perchloric acid in aq. soln. reddens without bleaching blue litmus. Perchloric acid is a strong monobasic acid which forms normal salts—perchlorates—of the type $MClO_4$; with lead and bismuth oxides it forms what are considered to be basic perchlorates; but no acid salts are known. The perchlorates are in general soluble in water, but the alkali perchlorates are among the least soluble of the perchlorates, and on thi fact is based a method for the gravimetric determination of potassium in the presence of sodium. Indeed, perchloric acid is replacing the use of hydrochloro-platinic acid for this purpose; the cost is much less, and the results are satisfactory. Most of the perchlorates are deliquescent; those of ammonium, potassium, lead, and mercury are not deliquescent. K. A. Hofmann[26] and his co-workers showed that perchloric acid has also a tendency to form crystalline compounds with many feeble organic bases—*e.g.* ammonium, carbonium, and oxonium salts.

The perchlorates and permanganates are isomorphous, and this points to a similarity in the structure of each. The perchlorates require a higher temp. for their decomposition than do the chlorates. The products are either oxygen with possibly a trace of chlorine and the metal chloride, or the oxide and a mixture of chlorine and oxygen gases. The perchlorates detonate when projected on to red-hot charcoal; when triturated with **sulphur** and charcoal; or when melted with reducing agents. The perchlorates are not decomposed below 100° by **sulphuric acid**; by fuming **hydrochloric acid**, hot or cold; and neither acid gives with perchlorates the yellow coloration furnished by the chlorates. Towards the b.p., 40 per cent. sulphuric acid decomposes perchlorates into oxygen and chlorine. Boiling conc. **nitric acid** or fuming nitric acid decomposes potassium perchlorate. Perchloric acid, in combination, is the most stable of the oxygen acids; and D. Vitali has shown that in soln., the perchlorates are scarcely affected by the strongest reducing agents, which readily reduce the chlorates. D. Tommasi[27] found that potassium perchlorate soln. are not attacked by **zinc** or **magnesium** in acid or in cupric sulphate soln.; but perchlorates are easily reduced by **thiosulphates** without the evolution of hydrogen. J. G. Williams found that the perchlorates are reduced by **titanium trichloride,** while the chlorates are not affected, and based a process for the volumetric determination of perchlorates—in the presence of chlorates or chlorides—on this reaction. On the other hand, H. Eccles found that an aq. soln. of potassium chlorate is reduced by the **copper-zinc couple,** while potassium perchlorate is not. O. Loew and K. Aso found potassium perchlorate is reduced in the presence of **platinum black** and glucose. T. Fairley detected no action between the perchlorates and **hydrogen peroxide.** C. Zenghelis found that potassium perchlorate in aq. soln. is reduced by **hydrogen** generated in an external vessel and passed into the soln. through filter-paper or parchment. Several metals are attacked by fused perchlorates as by fused chlorates.

The detection and determination of the perchlorates.—The perchlorates give no precipitates with silver nitrate or barium chloride soln.; conc. soln. give a white crystalline precipitate with potassium chloride. Unlike all the other oxy-acids of chlorine, a soln. of indigo is not decolorized by perchloric acid, even after the addition of hydrochloric acid; and they do not give the explosive chlorine dioxide when warmed with sulphuric acid; unlike the chlorates, the perchlorates are not reduced by the copper-zinc couple, or sulphur dioxide. Perchloric acid can be titrated with $\frac{1}{10}N$-alkali, using phenolphthalein as indicator. The perchlorates can be converted into chlorides by heat and the chlorides determined volumetrically or gravimetrically; they can be reduced to chloride by titanous sulphate[28] and titration of the excess of titanous sulphate with standard permanganate; they can be fused with zinc chloride and the amount of chlorine liberated can be measured in terms of the iodine set free from a soln. of potassium iodide; and they can be

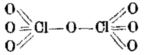
heated to 200° with metaphosphoric acid and potassium iodide, and the iodine set free is eq. to the perchlorate decomposed.[29]

The composition and constitution of perchloric acid.—The composition of perchloric acid was established by F. von Stadion,[30] and verified by J. L. Gay Lussac by the decomposition of potassium chlorate. 10·03 grams of perchloric *acid were dissolved in water, and treated with a small excess of potassium carbonate.* The soln. was evaporated to dryness with a slight excess of acetic acid, and washed with absolute alcohol to remove the potassium acetate. The residual potassium perchlorate was dried and weighed. The potassium perchlorate was ignited to drive off the oxygen. The results were:

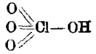
Potassium perchlorate	13·8326 grms.
Potassium chloride, KCl	7·4434 ,,
Oxygen	6·3892 ,,

The composition of the residual potassium chloride, by a previous analysis, is known to be KCl with a mol. wt. 74·56. Divide the amount of oxygen by 16, and the amount of potassium chloride by 74·56, to get the atomic ratio KCl : O. This was ound to be KCl : O = 1 : 4, corresponding with the empirical formula $KClO_4$ *for the potassium salt, and $HClO_4$ for the acid. If the acid is monobasic the formula* must be $HClO_4$; if dibasic, $H_2Cl_2O_8$, etc. If the acid is dibasic, it would *probably* be possible to prepare an acid salt, $KHCl_2O_8$. The acid salt has not been made, hence the analytical data may be taken as circumstantial evidence that the molecular formula of the salt is $KClO_4$. Thus, **it is possible to estimate the probable molecular formula of an acid by chemical analysis, and, mutatis mutandis, also of the base.** By the same argument it has been shown that the formula of hydrofluoric acid is probably H_2F_2, because it behaves as a dibasic acid. If this argument were of general application it would be inferred that hyposulphurous acid is monobasic HSO_2, because only one series of salts are known. This acid is, however, generally supposed to be dibasic, $H_2S_2O_4$. Consequently, it must not be supposed that an acid must be monobasic because it is known to furnish but one series of normal, and no acid salts, because acids are known which give no acid salts and are undoubtedly dibasic.

F. M. Raoult[31] found that the mol. wt. of potassium perchlorate, determined by the raising of the b.p. of alcohol, agreed with the simple formula $KClO_4$; and a similar result was deduced by J. M. Crofts from the effect of sodium chlorate on the f.p. of sodium sulphate. W. Ostwald's values by the specific conductivity method gives $\lambda 1024 - \lambda 32 = 13·6$ for potassium chlorate, consonant with the value for monobasic acids. The great stability of the perchlorates, as with the chlorates, in comparison with the other oxy-acids of chlorine makes the chain formula H—O—O—O—O—Cl appear almost irrational, since such a compound would be unstable. C. W. Blomstrand's formula makes chlorine a heptad in chlorine heptoxide, Cl_2O_7, and in perchloric acid, $HClO_4$,

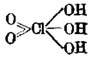


Chlorine heptoxide Cl_2O_7.

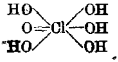


Perchloric acid, $HClO_4$.

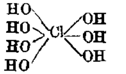
The same formula makes G. S. Sérullas' hydrate, $HClO_4.H_2O$; the dihydrate, $HClO_4.2H_2O$; and the trihydrate, $HClO_4.3H_2O$, respectively:



Monohydrate, $HClO_4.H_2O$.



Dihydrate, $HClO_4.2H_2O$.



Trihydrate, $HClO_4.3H_2O$.

but since no salts are known to correspond with these assumptions, the hypotheses are not of much value. The septivalency of chlorine assumed to explain the structure of perchloric acid and of its anhydride, agrees with the univalency of chlorine in hypochlorous acid, Cl.OH ; the tervalency of chlorine in chlorous acid, O=Cl—OH ; its quinquevalency in chloric acid, $O_2\equiv Cl-OH$; and its septivalency in perchloric acid.[32]

The higher the active valency of the halogen oxides the greater their stability. Thus, perchloric acid is the most stable of all the oxyacids of chlorine. Similarly iodine pentoxide is more stable than the lower oxides of iodine. Allied phenomena occur with many other elements. Thus, each atom of chlorine in gold trichloride is attracted with a greater force than the single chlorine atom in gold monochloride, AuCl, as is illustrated by the heats of formation of the two compounds per atom of chlorine—thus $\frac{1}{3}$[Au, Cl_3]=7·6 Cals. ; [Au, Cl]=5·8 Cals. In many other cases, the converse is true, and the higher the active valency of an element the feebler its attractive power for other atoms. Thus, sexivalent chromium in chromic trioxide, CrO_3, and tervalent chromium in chromium sesquioxide, Cr_2O_3 ; the heats of formation of the two compounds per atom of oxygen are respectively 46·7 Cals. and 89·3 Cals. The former breaks down at about 190°, and the latter does not part with its oxygen at 1600°.

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§ 15. Perbromic Acid and the Perbromates

No reaction is known which offers the slightest evidence that bromine or iodine is capable of directly replacing chlorine in its oxy-acids; and from a theoretical point of view, such a reaction, implying as it does the direct substitution of an element joined to a number of oxygen atoms, is exceedingly improbable.—A. MICHAEL AND W. T. CONN.

Several attempts have been made to prepare a perbromic acid, $HBrO_4$, analogous to perchloric acid, $HClO_4$, but all the announcements[1] which have been made respecting the preparation of this acid have not withstood the ordeal of adverse criticism. In 1863, H. Kämmerer said that perbromic acid can be made by the action of dry bromine vapour on the vapour of perchloric acid, provided no chlorous acid is present. The claim was denied by E. MacIvor in 1876, by G. Wolfram in 1899, and by A. Michael and W. T. Conn in 1901. Bromine is without action on perchloric acid, perchloric anhydride, or silver perchlorate, even when the mixture is heated in sealed tubes. M. M. P. Muir (1874) thought he had made it by shaking bromine with an aq. soln. of perchloric acid, but a couple of years later, he showed that he had been mistaken. P. W. Robertson (1912) found no signs of the formation of a perbromate by the action of bromine on potassium perchlorate, or on sodium periodate even when the operations were performed in sealed tubes at 100° or 250°. Lead peroxide reduces potassium bromate to the bromide, although its presence facilitates the conversion of potassium chlorate to perchlorate. S. Tanatar (1899) also showed that hydrogen peroxide reduces bromic acid to hydrobromic acid. E. H. Cook also failed to find the slightest trace of perbromate in the products of the decomposition of potassium bromate by heat. E. Müller and O. Friedberger (1902) failed to obtain perbromic acid by electrolytic processes which succeeded with

the perchlorates and periodates. Neither perbromic acid nor its salts have yet found a permanent place in the list of known chemical compounds. There is no known difference between the valency of bromine and chlorine or iodine which accounts for the non-success of the attempts to prepare perbromic acid or the perbromates. Hence, says P. W. Robertson:

It seems probable that within a molecule there are in operation forces of attraction and repulsion, dependent on the mass and nature of the component atoms, causing inter-molecular vibrations of greater or less intensity. In the case of a molecule such as $HBrO_4$, the vibrations would be so intense that such a system of atoms would not be capable of existence.

The alleged substitution of chlorine by bromine or iodine in the oxy-acids of chlorine.—N. A. E. Millon [2] showed in 1843 that when iodine is heated with a soln. of potassium chlorate and a small quantity of nitric acid, potassium iodate is formed; and in 1834, A. J. Balard found that, contrary to expectation, hypochlorous acid will react with bromine to form bromic acid, because in the mutual displacement of chlorine, bromine, and iodine in the haloid salts and acids, the electro-negative tendency of bromine is much less than that of chlorine. A. J. Balard could not oxidize bromine by a conc. soln. of chloric acid, or chlorine dioxide, although H. Davy had made iodic acid by heating iodine with chlorine dioxide, as well as with chlorine monoxide or hypochlorous acid. H. Kämmerer's reports of *successful substitutions of chlorine by bromine—e.g. the formation of bromic* acid from bromine and chloric acid; the formation of perbromic acid by the action of bromine on the vapour of perchloric acid; and the formation of periodic acid by heating a conc. soln. of perchloric acid with iodine—lack confirmation. This agrees with J. Thomsen's observation (i) that the heat of formation of aq. bromic acid is considerably less than that of aq. chloric acid; and (ii) that the direct replacement of chlorine in chloric and perchloric acids by iodine is more probable from a thermochemical point of view than by bromine, for the heat of formation of the oxy-acids of iodine is considerably greater than the corresponding chlorine acids. The alleged formation of periodic acid from perchloric acid and iodine, has never led to the formation of a higher state of oxidation than iodic acid; hypochlorous and chloric acids have been used, and these are more vigorous oxidizing agents than perchloric acid. Similarly, when iodine and chlorine heptoxide react in the cold, iodine pentoxide will be formed as a fuming white powder—provided an explosion does not occur during the reaction. The formation of bromic or iodic acid by the action of bromine or iodine on chloric acid is more probably an oxidation than a substitution process.

Bromine is not acted on by nitric acid, chlorous acid, potassium permanganate, lead or mercury oxides, etc., hot or cold perchloric acid—even when the mixture is exposed to sunlight; nor does bromine react with chlorine heptoxide. Consequently, it is probable that the replacement of chlorine by bromine or iodine in several reactions admits of a different interpretation—namely, oxidation. Thus, (*a*) the formation of bromic acid by the action of aq. hypochlorous acid and bromine under conditions where chloric acid is without action, is attributed by A. Michael and W. T. Conn to the tendency of hypochlorous acid to pass into chloric acid through the agency of water: $HOCl+2H_2O=HClO_3+2H_2$, followed by $H_2+HOCl=HCl+H_2O$. The presence of bromine favours the decomposition of water with the formation of hydrobromic acid, which reacts with hypochlorous acid, forming bromine chloride, which, in the presence of water and chlorine formed by the interaction of hydrochloric and hypochlorous acid, is converted into bromic acid. The failure of chloric acid to effect the oxidation of bromine indirectly turns on the fact that this acid does not pass into perchloric acid so readily as hypochlorous acid passes into chloric acid. (*b*) The formation of bromic or iodic acid by the action of bromine or iodine on aq. potassium chlorate is explained by A. Potilitzin by assuming that the reaction between chlorine and sodium bromate: $5NaBrO_3+3Cl_2+3H_2O$

$=5NaCl+5HBrO_3+HClO_3$, proceeds more readily than the reaction between bromine and sodium chlorate: $5NaClO_3+3Br_2+3H_2O=5NaBr+5HClO_3+HBrO_3$. Neither reaction proceeds by direct substitution, for the formation of bromic acid is due to the greater affinity of sodium for bromine than for the ClO_3-radicle; this causes a decomposition with the intervention of water, and the formation of hypobromous acid which is oxidized to bromic acid. *The reaction is thus essentially the same in character as the formation of sodium bromate from bromine and sodium* hydroxide.

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§ 16. Periodic Acid and the Periodates

Periodic acid was discovered by F. Ammermüller and G. Magnus[1] about 1833, and described in their paper *Ueber eine neue Verbindung des Jods mit Sauerstoff—die Ueberjodsäure*. *Periodic anhydride* or *iodine heptoxide*, I_2O_7, corresponding with A. Michael and W. T. Conn's perchloric anhydride, Cl_2O_7, has not been definitely isolated. M. Bengieser's claim to have made it by heating the hydrate to 160° was contradicted by C. Langlois and C. F. Rammelsberg, who showed that iodine pentoxide, I_2O_5, not iodine heptoxide, I_2O_7, is formed under these conditions. A. B. Lamb's attempt to prepare periodic anhydride by treating periodic acid with acetyl chloride, acetic anhydride, or anhydrous perchloric acid proved futile; and the product obtained by A. Michael and W. T. Conn by treating chlorine heptoxide with iodine, at first thought to be iodine heptoxide, was really iodine pentoxide. J. Ogier's mixture of oxides, obtained by the action of electric sparks on a mixture of iodine vapour and oxygen, is said to contain iodine heptoxide, but this has not been established.

The nomenclature of the periodic acid and the periodates.—The periodates form a complex series of salts[2] most of which can be regarded as derivatives of acids genetically related with the hypothetical *periodic anhydride*, that is *iodine heptoxide*, I_2O_7, by replacing the oxygen atoms, one by one, with eq. hydroxyl groups, as illustrated in Table III. When one anhydride forms a series of acids by union with different amounts of water, the acid containing most water is called the **ortho-acid**—from the Greek ὀρθός, regular; the other acids have prefixes, making **para-acid**—from the Greek παρά, beside; **meso-acid**—from the Greek μέσος, middle, intermediate; and **meta-acid**—from the Greek μετά, beyond, less than the highest. The **di-acids** are supposed to be formed by the abstraction of one molecule of water from two molecules of acid. What is here called *para-periodic acid* is often regarded as *ortho-periodic acid*, on the assumption that the periodic acids have a quinquevalent nucleus or IO-group, thus making $IO(OH)_5$ orthoperiodic acid; $IO_2(OH)_3$, meso-periodic acid; and $IO_3(OH)$, meta-periodic acid. The last two terms correspond with those indicated in Table III.

It will be evident that if the acids are polybasic, we can imagine available hydrogen atoms replaced one by one. If all the available hydrogen atoms are replaced by bases, the **normal salt** is obtained; if only *one* of the available hydrogen

atoms is replaced, the **primary salt**; if two, the **secondary salt**; if three, the **tertiary salt**; if four, the **quaternary salt**; if five, the **quinqinary salt**; etc. For example,

TABLE III.—THE PERIODIC ACIDS.

I_2O_7 with	Compounds formed.	Empirical formula of acid.	Name of acid.	Salts.
$7H_2O$	$I_2(OH)_{14}$; or $2I(OH)_7$	H_7IO_7	Ortho-periodic acid	No salts known.
$6H_2O$	$I_2O(OH)_{12}$	$H_{12}I_2O_{13}$	Diortho-periodic acid	Salts have been reported; probably mixtures.
$5H_2O$	$I_2O_2(OH)_{10}$; or $2IO(OH)_5$	H_5IO_6	Para-periodic acid	Ag_5IO_6; $Ag_2H_3IO_6$; etc.
$4H_2O$	$I_2O_3(OH)_8$	$H_8I_2O_{11}$	Dipara-periodic acid	Salts have been reported; probably mixtures.
$3H_2O$	$I_2O_4(OH)_6$; or $2IO_2(OH)_3$	H_3IO_5	Meso-periodic acid	Ag_3IO_5; $Pb_3(IO_5)_2$; etc.
$2H_2O$	$I_2O_5(OH)_4$	$H_4I_2O_9$	Dimeso-periodic acid	$K_4I_2O_9$
$1H_2O$	$I_2O_6(OH)_2$; or $2IO_3OH$	HIO_4	Meta-periodic acid	KIO_4; $AgIO_4$; etc.

if M be used to represent a univalent atom or radicle, the various salts of para-periodic acid H_5IO_2 would be represented:

Normal.	Primary.	Secondary.	Tertiary.	Quaternary.
$IO(OM)_5$	$IO(OM)(OH)_4$	$IO(OM)_2(OH)_3$	$IO(OM)_3(OH)_2$	$IO(OM)_4(OH)$
M_5IO_6	MH_4IO_6	$M_2H_3IO_6$	$M_3H_2IO_6$	M_4HIO_6

The preparation of periodic acid and the periodates.—The most general and important method of preparing periodic acid depends on the oxidation of iodates in alkaline soln. by means of chlorine: $NaIO_3+3NaOH+Cl_2=Na_2H_3IO_6+2NaCl$. This method was used by F. Ammermüller and G. Magnus,[3] the discoverers of this acid, and C. W. Kimmins has shown that if the soln. is sat. in the cold, sparingly soluble secondary sodium paraperiodate, $Na_2H_3IO_6$, is formed, but if the mixture is boiling, tertiary sodium paraperiodate, $Na_3H_2IO_6$, is formed; and at intermediate temp. mixtures of these two salts are obtained. According to J. Philipp, if potassium hydroxide and iodate are used, potassium chlorate, and potassium meta-periodate, KIO_4, are produced: $KIO_3+2KOH+Cl_2=KIO_4+2KCl+H_2O$. If the molecular ratio of KOH to KIO_3 in the soln. be 3 : 1, not quite two-thirds of the quantities represented by this equation are obtained; if the molecular ratio be 2 : 1, less than half these quantities are produced; while if chlorine acts on potassium iodate alone, only a small quantity of periodate is formed. If potassium iodate soln. is evaporated, G. Magnus and F. Ammermüller say the product is $K_4I_2O_9$, while C. W. Kimmins makes it $K_3HI_2O_9$.

A brisk current of chlorine is led into a boiling 10 per cent. soln. of alkali lye containing the eq. of 60 grms. of sodium hydroxide, and in which 12·7 grms. of finely powdered iodine are suspended; when the precipitate which is suddenly formed begins to cause bumping, the flame is removed, and the current of chlorine continued until no more white precipitate of $Na_2H_3IO_6$ is formed. While the liquid is still warm, the precipitate is collected on a Büchner's funnel, and thoroughly washed with cold water, and dried in a steam-bath. An 80 per cent. yield or 22 grms. of the salt are obtained. The sodium salt is converted into silver periodate by suspending it in a boiling dil. soln. containing the eq. of 3 mol. of silver nitrate, the liquid is boiled, filtered hot, and the black precipitate of silver iodate, Ag_3IO_5, washed with water. The filtrate contains some nitric acid, and some silver periodate, $Ag_2H_3IO_6$. The silver iodate can be recovered from the filtrate by evaporation to a small volume, and, on cooling, golden-yellow crystals of $Ag_2H_3IO_6$ separate out. H. L. Wells[4] now obtains the acid by suspending the moist silver iodate in a little water, and leading in chlorine gas, with agitation, until the precipitate is almost white. The silver chloride can then be removed by filtration. The filtrate when conc. first on a water-bath, and then over conc. sulphuric

acid, gives a crop of crystals of periodic acid. According to H. Kämmerer, bromine acts better than chlorine, because if any bromic acid is formed, it is completely decomposed by evaporation without leaving any residue.

The oxidation of iodate to periodate can also be effected by adding an excess of hypochlorite instead of chlorine.[5] C. F. Rammelsberg[6] made the periodates by the calcination of the iodates of the alkaline earths: $5Ba(IO_3)_2=Ba_5(IO_6)_2+4I_2+9O_2$, but E. H. Cook obtained no periodate during the calcination of the alkali iodates. C. F. Rammelsberg also oxidized barium iodide by heating a mixture of it with barium peroxide: $BaI_2+8BaO_2=Ba_5(IO_6)_2+4BaO$; iodine may be used in place of the iodide: $2I_2+6BaO_2=Ba_5(IO_6)_2+BaI_2$. C. Rammelsberg assumed that the periodate is not formed during the ignition, but afterwards when the mass is treated with water. When an intimate mixture of sodium peroxide and iodine is touched with the tip of a red-hot wire, the whole mass becomes incandescent, and a mixture of sparingly soluble periodate and soluble sodium iodate is formed. The latter with the uncombined iodine are leached out by water. Barium calcium or strontium paraperiodate is also made by heating the corresponding iodate alone: $5Ba(IO_3)_2=Ba_5(IO_6)_2+4I_2+9O_2$. C. F. Rammelsberg also obtained barium iodate by heating barium iodide in a stream of air up to the point at which it begins to develop iodine vapour: $5BaI_2+6O_2=Ba_5(IO_6)_2+4I_2$. C. F. Cross and S. Seguira found that the periodates are also made by heating carbonates or oxides in a stream of iodine vapour, but, according to J. C. G. de Marignac, not by the action of oxygen on heated iodates. Similarly, M. Höhnel obtained sparingly soluble sodium periodate, $Na_2H_3IO_6$, by the action of sodium peroxide upon iodine suspended in water. According to E. H. Riesenfeld and F. Bencker, ozone is without action on acid or neutral soln. of potassium iodate, but alkaline soln. are oxidized to periodates. Ozone is without action on periodates. According to E. Péchard, ozone converts potassium iodide into the periodate, which then reacts with the excess of potassinm iodide, forming the iodate. According to V. Augur, the idea that ozone acting upon a soln. of potassium iodide forms periodate has arisen from the idea that iodine is liberated from a mixture of potassium iodide and periodate but not from a mixture of the iodide and iodate, whereas iodine is liberated by carbon dioxide from the last-named mixture unless a large excess of sodium bicarbonate is present. The test for the periodate is therefore vitiated unless precautions be taken to exclude carbon dioxide. J. Philipp oxidized iodine trichloride in boiling water containing an excess of finely-divided silver oxide in suspension, and E. Preuss oxidized iodine by adding it to molten silver nitrate.

H. Kämmerer[7] believed that iodine and chlorine exchanged places when an aq. soln. of perchloric acid is heated with iodine: $2HClO_4+I_2+4H_2O=2H_5IO_6+Cl_2$. The chlorine may be expelled by warming the liquid in a water-bath. The action proceeds more rapidly the more conc. the perchloric acid: A. Michael and W. T. Conn could get no periodic acid by the process indicated by H. Kämmerer, and it is believed that the reaction really involves an oxidation of the iodine by the perchloric acid. As is generally the case with acids and their salts, many periodates are obtained by the direct action of periodic acid on the hydroxides or carbonates of the metals, and by the treatment of soln. of the alkali periodates with salts of the metals which give sparingly soluble periodates—*e.g.* silver, barium, lead, copper, cadmium, mercury, nickel, iron, etc. Similarly, a soln. of the acid is obtained by the action of sulphuric acid on barium periodate (F. Selmons),[8] or lead periodate (M. Bengieser); or of chlorine or bromine on silver metaperiodate, $AgIO_4$ (H. Kämmerer).

The sparingly soluble secondary sodium paraperiodate, $Na_2H_3IO_6$, readily dissolves in dil. nitric acid, and F. Ammermüller and G. Magnus added silver nitrate to the cold soln. and obtained an orange-yellow precipitate of secondary silver paraperiodate, $Ag_2H_3IO_6$. The precipitate was dissolved in hot dil. nitric acid and conc. on a water-bath where orange-coloured crystals of silver metaperiodate, $AgIO_4$, were precipitated: $2Ag_2H_3IO_6+2HNO_3=2AgIO_4+2AgNO_3+2H_2O$. The crystals were collected and when treated with cold

water paraperiodic acid, H_5IO_6, and secondary silver paraperiodate, $Ag_2H_3IO_6$, were formed in accord with the equation: $2AgIO_4+4H_2O=H_5IO_6+Ag_2H_3IO_6$. The periodic acid crystallizes from the clear liquid after it has been conc. on the water-bath, and evaporated over sulphuric acid in vacuo.

C. W. Kimmins'[9] study of the periodates of silver has shown that the composition of the precipitate depends upon the concentration of the nitric acid in which the sodium periodate is dissolved when the silver nitrate is added. If the amount of nitric acid be just sufficient to effect the dissolution of the sodium salt, a dark brown precipitate of secondary silver mesoiodate, Ag_2HIO_5, is formed; if but a slight excess of nitric acid is used dark-red secondary silver paraperiodate is formed, $Ag_2H_3IO_6$; if a further excess of nitric acid is used, slate-coloured tertiary silver paraperiodate, $Ag_3H_2IO_6$, is formed; and if conc. nitric acid be used in excess, monohydrated silver metaperiodate, $AgIO_4.H_2O$, is formed in orange crystals.

Periodic acid and the periodates are formed by the electrolysis of soln. of iodic acid on the iodates or iodides,[10] but if the electrolysis be conducted in a cell without a diaphragm, no hydrogen is evolved because it is all used in reducing the iodate, and after the electrolysis has proceeded for some time, the evolution of oxygen also ceases. Any further electrolysis does not alter the ratio of the iodide to iodate, for as fast as iodate is formed on the anode it is reduced on the cathode. Neutral soln. of iodates are not oxidized to periodates, and in alkaline soln. the presence of potassium chromate does not prevent the cathode reduction of iodate to iodide. E. Müller electrolysed a 50 per cent. soln. of iodic acid confined as anode liquid either in a porous cell, or by means of an earthenware diaphragm. A $2N$-H_2SO_4 soln. was used as cathode liquid. The cathode was a piece of platinum foil, the anode is either made of platinum or a lead tube coated with lead peroxide. A current density of 0·8 amp. per sq. dm., and 1 to 3 volts at a temp. of 8°–9°. Iodates in soln. rendered alkaline with 4 per cent. of sodium hydroxide can also be used as anode liquid. A 25 per cent. yield is then obtained. The electrolysis of an alkaline soln. of potassium iodate gives a precipitate of potassium periodate, KIO_4; sodium iodate, a precipitate of $Na_2H_3IO_6$. A low current density and low temp. increase the yield. The yield is also augmented to some extent by the use of chromates.

The properties of periodic acid and the periodates.—According to C. F. Rammelsberg,[11] **paraperiodic acid,** H_5IO_6, *i.e.* $IO(OH)_5$, separates from its aq. soln. as deliquescent colourless prisms which resemble gypsum, and are probably monoclinic. The crystals melt according to M. Bengieser at 130°; according to A. Rosenheim and E. Löwenthal, between 129° and 130°; and according to C. Langlois, at 134°±4·5°. E. Löwenthal says that the acid begins to decompose between 121° and 122°, and that the m.p. is somewhat obscured in consequence. According to C. F. Rammelsberg, the molten acid begins to decompose between 133° and 138°, and at 138°–140° decomposition is complete; the products are water, ozonized oxygen, and iodine pentoxide. M. Bengieser thought that at 160° the molten acid forms periodic anhydride, I_2O_7, which passes into iodine pentoxide, I_2O_5, at 190°; but these statements were contradicted by C. G. Lautsch, C. Langlois, and C. F. Rammelsberg. By heating paraperiodic acid for 20 to 25 hrs. under reduced press. (12 mm.) at 100°, that is, until the weight is constant, A. B. Lamb obtained a white residue whose composition corresponded with normal periodic acid, HIO_4, and which is therefore **meta-periodic acid,** HIO_4. The product dissolves in water with a hissing noise, sublimes at 110°, and at 138° furnishes iodine pentoxide, I_2O_5. The intermediate *meso-periodic acid*, H_3IO_5, was not observed. A. Rosenheim and E. Löwenthal found that periodic acid resembles telluric acid more than it does perchloric acid, and the periodates are more like tellurates than they are like perchlorates.

According to C. Langlois, periodic acid is slightly soluble in alcohol, less soluble in ether, and very soluble in water. The aq. soln. is colourless and has an acid reaction. According to J. Thomsen,[12] the **specific volume**, v, of aq. soln. of the

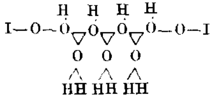
composition $H_5IO_6+nH_2O$ at 17° is $v=59{\cdot}6+18n$; and the **specific gravity**, S, at the same temp. $(59{\cdot}6+18n)S=228+18n$:

n	20	40	80	160	320 H_2O
S	1·4008	1·2165	1·1121	1·0570	1·0288
Volume difference	59·8	59·3	60·0	60·2	60·0 c.c.

where the last line represents the difference in volume between the soln. and solvent calculated per mol. of solute, H_5IO_6. The **molecular heat of solution** in 240 mol. of water is −1·38 Cals.; the **heat of formation** from its elements is: $I_{solid}+6O+5H=H_5IO_{6solid}+185{\cdot}78$ Cals.; and in soln.: $I_{solid}+6O+5H+Aq.=H_5IO_{6aq.}+184{\cdot}4$ Cals.: and for $I_{solid}+4O+H+Aq.=HIO_{4aq.}$ J. Thomsen gives 47·68 Cals., and M. Berthelot, 53·5 Cals. The **heat of neutralization**, as with the heat of soln., increases step by step with increasing amounts of alkali. According to J. Thomsen, the heat of neutralization, Q, of a mol of paraperiodic acid, H_5IO_6, by n mol. of potassium hydroxide—all in soln.—is

n	1	1·5	2	2·5	3	5 KOH
Q	51·5	16·56	26·59	29·23	29·74	32·04 Cals.
	Acid.	Neutral.	Alkali soln.			

Consequently the addition of the first mol. of KOH furnishes 5·15 Cals.; the second, 21·44 Cals.; the third, 3·15 Cals.; and the fourth and fifth, 2·3 Cals. *The mean of the first two values is 13·195, corresponding with the normal value for strongly ionized acids. This is said to be a chance result.* J. Thomsen *infers that* periodic acid is dibasic, and writes the formula $IO_4H_3(OH)_2$; or better still tetrabasic $I_2O_8H_6(OH)_4$, and he writes the formula—oxygen quadrivalent, iodine univalent—



A. Basarow and L. Meyer objected to J. Thomsen's hypothesis. A. Basarow[13] regards iodine as septivalent and assumes paraperiodic acid to contain five hydroxyl groups, $(HO)_2:IO:(HO)_3$, two of which behave as acidic hydroxyls, and three as alcoholic hydroxyls.

The **molecular conductivity** of periodic acid in soln. containing one mol. in v litres of water has been determined by W. Ostwald,[14] A. Rosenheim, and E. Löwenthal. The two sets of determinations are concordant. F. Kohlrausch gives 48 and 64 for the mobilities of the IO_4' and ClO_4'-ions respectively on the assumption that this ionization is: $HIO_4=H^{\cdot}+IO_4'$, the calculated ionization constant K does not change much with dilution. Assuming the mobility of the hydrogen is 338 at 25°, V. Rothmund and K. Drucker have calculated the degrees of ionization, α, and the ionization constants K, from W. Ostwald's eq. conductivities λ :

v	4	16	32	64	128	256	512	1024
λ	108	179	223	270	312	348	374	387
α	0·273	0·452	0·563	0·682	0·788	0·880	0·945	0·978
K	0·0256	0·0234	0·0227	0·0229	0·0229	0·0252	0·0310	0·0425

The value of K is fairly constant between $v=8$ and $v=128$, but it increases with still greater dilutions, possibly owing to an increase in the strength of the acid formation of more complex molecules. The conductivity measurements do not decide whether periodic acid is to be regarded as a binary electrolyte with anions IO_4' or hydrated anions H_2IO_5' or H_4IO_6'.

A. Rosenheim and E. Löwenthal measured the effect of periodic acid on the b.p. and f.p. of water. They found :

Grms. H_5IO_6 in 25 grms. water	0·5696	3·369	0·2808	1·3342	4·8104
Elevation of b.p.	0·10°	0·51°	—	—	—
Depression of f.p.	—	—	0·148°	0·648°	2·138
Mol. wt.	118·3	137·4	173·2	190·4	208·1

The theoretical mol. wt. for H_5IO_6 is 227·96. The ebulliscope measurements show that the acid is probably ionized like a binary electrolyte : $H_5IO_6 \rightleftharpoons H^{\cdot} + H_4IO_6{}'$ in boiling aq. soln., while the cryoscopic measurements of the 5 per cent. soln. show that the ionization is not so very marked, and becomes very small with the 12 to 20 per cent. soln. Taken in conjunction with the conductivity measurements, these results are taken to show that polymerized molecules are probably present in the cold soln. This conclusion is in accord with the results obtained with telluric acid.

A. Rosenheim and E. Löwenthal determined the concentration of the hydrogen ion in 0·05*N*-soln. of H_5IO_6, NaH_4IO_6, and $Na_2H_3IO_6$ by S. P. L. Sörensen's indicator method, and found respectively 6×10^{-3}, $4·05\times10^{-7}$, and $6·5\times10^{-10}$. By comparison with the value for 0·01*N*-HCl—$4·3\times10^{-3}$, and for *N*-acetic acid, $9·7\times10^{-4}$, it follows that periodic acid is intermediate between strong hydrochloric acid and weak acetic acid.

F. Ammermüller and G. Magnus[15] made no attempt to determine the basicity of the *Ueberjodsäure* which they had discovered. From the behaviour of the acid at a high temp., C. Langlois and C. G. Lautsch inferred that periodic acid is pentabasic ; and from his study of silver periodate, F. W. Ferlunds regarded the acid as tribasic. In the attempt to find the **basicity** of periodic acid, W. Ostwald[16] expressed his belief that his measurements of the electrical conductivity of soln. of periodic acid agreed better with the assumption that this acid is polybasic rather than monobasic ; but P. Walden's determinations with monosodium periodate show that this is the neutral salt of a monobasic acid : $\lambda_{1024}-\lambda_{32}=11·3$ at 25° ; and P. Walden regards the salts in which the ratio Na : I=2 : 1 are not dibasic salts, but rather salts of *dimesoperiodic acid*, $H_4I_2O_9$, which he calls *Pyroperjodsäure*, and salts containing five atoms for one molecule of the hydrate H_5IO_6, *basische Salze*. On the other hand, A. Rosenheim and O. Liebknecht say that with feeble bases like silver, periodic acid behaves like a pentabasic acid, while with strong bases it behaves like monobasic metaperiodic acid, HIO_4, a view which F. Giolitti believes is supported by the behaviour of the copper periodates which make periodic acid pentabasic, while the lead periodates make this acid tribasic. Hence, added F. Giolitti, *the normal basicity of periodic acid cannot be decided from chemical considerations alone.*

While perchloric acid behaves as a monobasic acid when titrated with litmus, methyl orange, or phenolphthalein as indicator, periodic acid is monobasic only when titrated with methyl orange since with the other indicators the changes of colour are gradual and indistinct. F. Giolitti[17] also found periodic acid to be monobasic towards sodium hydroxide with methyl orange as indicator, but dibasic when the neutral point is determined electrometrically. R. Dubrisay has also shown by a surface tension method that periodic acid behaves towards alkalies as a tribasic acid. A. Rosenheim and E. Löwenthal have shown that by using methyl orange as indicator, periodic acid can be quantitatively converted by titration into NaH_4IO_6, and by using thymol phthalein as indicator, it can be converted into $Na_2H_3IO_6$.

E. Cornec[18] has shown that the lowering of the f.p. of the soln. of periodic acid and sodium or potassium hydroxides cannot be followed throughout owing to the low solubilities of some of the salts. The curves showing the relation between the depression of the f.p. and the proportion of alkali show breaks corresponding with acid : base as 1 : 1, 1 : 2, and 1 : 3 for potassium and sodium salts, and 1 : 1 and 1 : 2 for ammonium salts. When an aq. soln. of periodic acid is treated with sodium hydroxide, the first action appears to be a neutralization of the acid molecules,

HIO_4, forming $NaIO_4$; as more sodium hydroxide is added, the $NaIO_4$ molecules are transformed into the neutral salt, $Na_4I_2O_9$, of the unknown acid $H_4I_2O_9$. This salt is sparingly soluble, and separates from the soln. Similar phenomena are observed with potassium hydroxide, but the potassium salt, $K_4I_2O_9$, is fairly soluble, and further additions of potassium hydroxide lead to the formation of a neutral salt, K_3IO_6, and when all is converted, subsequent additions of alkali give a soln. containing mixtures of K_3IO_6 and KOH. Hence, successive additions of alkali to a soln. of *periodic acid furnish neutral salts corresponding with three different* periodic acids: HIO_4, $H_4I_2O_9$, and H_3IO_6. Hence, J. Thomsen's data for the *thermal changes which occur when potassium hydroxide acts upon periodic acid*—where with the first mol. 5·15 Cals. are evolved; 21·5 Cals. with the second; and 3·1 Cals. with the third—refer not to the simple neutralization of a polybasic acid, but rather to the evolutions of heat in three totally different reactions.

The electrical conductivities—W. Ostwald and P. Walden's rule—the lowering of the f.p., and the raising of the b.p. of the 1 : 1 periodates, correspond with the simple formulæ MIO_4 and $MClO_4$. Similar evidence for the corresponding acids shows that aq. soln. contain respectively the molecules HIO_4 and $HClO_4$, and that the so-called para-periodic acid, H_4IO_6, which crystallizes from soln. of periodic acid is a dihydrate, $HIO_4.2H_2O$, which is more stable than the acid itself. This recalls the relatively great stability of the hydrates of perchloric acid.

Again, the electrical conductivities—W. Ostwald and P. Walden's rule—show that the simplest formula for the 1 : 2 periodates is $M_4I_2O_9$, and therefore the three known solid 1 : 2 periodates should not be formulated $Na_2H_3IO_6$; $K_2H_3IO_6$; and $(NH_4)_2H_3IO_6$, but rather $Na_4I_2O_9.3H_2O$; $K_4I_2O_9.3H_2O$; and $(NH_4)_4I_2O_9.3H_2O$ respectively. *This inference is in accord with the fact that the potassium salt loses* the eq. of nine molecules of water when dried over sulphuric acid; that the sodium *salt loses its three molecules of water at 200°; and the ammonium salt its three* molecules of water at 100°—all without decomposition. The lowering of the f.p. and the application of W. Ostwald and P. Walden's rule show that the most simple formula for the 1 : 3 periodates is M_3IO_5, and accordingly, the potassium and sodium salts are respectively $K_3IO_5.4H_2O$ and $Na_3IO_5.H_2O$.

Paraperiodic acid does not lose in weight when dried at 100°, or over con. sulphuric acid. *According to A. B. Lamb,*[19] *when paraperiodic* acid, H_5IO_6, or what is considered to be the same thing, $HIO_4.2H_2O$, is heated to 110° under ordinary press., or at 100° under a press. of 12 mm., it decomposes, and the residue has a composition corresponding with HIO_4; at 138°, there is much sublimation, and large quantities of iodine pentoxide, I_2O_5, are formed. Most of the periodates when heated up to about 300° lose oxygen, and are transformed into iodates; at a still higher temp., iodine and oxygen are evolved, and this the more the smaller the ratio of metal to acid. Some of the metaperiodates are inclined to decompose explosively, while the periodates of the stronger bases can be heated to redness *without decomposition. According to C. F. Rammelsberg, aq. soln. of periodic* acid or of sodium metaperiodate, acquire a pale yellow colour on standing, and give *a smell recalling that of ozone, while* P. Walden says that a $\frac{1}{4}N$-soln. of periodic acid develops the ozone smell after it has stood for an hour, and iodates are slowly formed; the decomposition is quicker if an acceptor for the oxygen be present—*e.g.* potassium iodide. W. Lenz and E. Richter could find no hydrogen peroxide in aq. soln. of periodic acid. Aq. soln. of the acid can be boiled without decomposition. According to S. Tanatar, hydrogen peroxide first reduces periodic to iodic acid, and then decomposes the latter; while, according to E. Müller, periodates are decomposed with the evolution of oxygen. Sodium periodate is slowly decomposed by hydrogen peroxide, forming sodium iodate with the liberation of oxygen. When a dil. soln. of periodic acid is similarly treated, the acid is completely reduced to iodic acid with the separation of only a trace of iodine; with a conc. soln., the reaction is incomplete and much iodine is separated. According to V. Auger, the salt $Na_4I_2O_9.3H_2O$ gives sodium iodate and a larger amount of oxygen than

corresponds with the reaction: $Na_2H_3IO_6+H_2O_2=NaIO_3+2H_2O+NaOH+O_2$, owing to the catalytic decomposition of the peroxide.

Periodic acid and the periodates act as energetic oxidizing agents and produce effects similar to those obtained with iodic acid. According to M. Bengieser, **phosphorus** is oxidized to phosphoric acid by periodic acid; **zinc** forms zinc oxide; **iron** forms ferric oxide; **copper** forms cupric iodate, $Cu(IO_3)_2$; while **mercury, tin,** and **lead** are only slightly attacked. C. F. Rammelsberg found that periodic acid or the periodates convert **ferrous oxide** into ferric iodate, and **manganous oxide** into hydrated manganese dioxide and manganous iodate; according to H. Kämmerer, **bismuth oxide,** Bi_2O_3, is oxidized to bismuth dioxide. D. Vitali has studied the effect of various **reducing agents** on the periodates and shown that they behave like the iodates. M. Bengieser found **acetic, formic, oxalic, and tartaric acids** to be slowly oxidized to water and carbon dioxide by periodic acid or by periodates, and E. Péchard found the reaction with oxalic acid proceeds rapidly if manganese sulphate, $MnSO_4$, be present; and O. Loew and K. Aso found potassium periodate is reduced by glucose. C. Langlois showed that periodic acid, and C. F. Rammelsberg that periodates, are immediately decomposed by **sulphur dioxide, hydrogen sulphide**, and conc. **sulphuric acid**. F. Selmons has published an investigation: *Ueber die Zeitdauer der Reaction zwischen Ueberjodsäure und Schwefligersäure* (Berlin, 1887) from which it would appear that the reaction proceeds: $H_2SO_3+HIO_4=H_2SO_4+HIO_3$; and also $4H_2SO_3+HIO_4=4H_2SO_4+HI$; and the hydriodic acid so formed is oxidized by the remaining periodic acid to iodine, for periodic acid was shown by C. F. Rammelsberg to be reduced by hydriodic acid or potassium iodide, with the separation of iodine. F. Ammermüller and G. Magnus also showed that **hydrochloric acid** is likewise reduced: $HIO_4+2HCl=HIO_3+H_2O+Cl_2$. Acid soln. of the metaperiodates are reduced in a similar way. According to E. Péchard, sodium metaperiodate behaves as if it were a compound of sodium iodate and active oxygen, for its soln. give the reaction of ozone. Thus **sodium iodide** is decomposed in the cold by a soln. of sodium periodate, iodine is liberated, and the liquid acquires an alkaline reaction with litmus: $2NaIO_4+2NaI+2H_2O=NaIO_3+Na_2H_3IO_6+NaO+I_2$; if the mixture is allowed to stand for some time, the alkaline soln. becomes neutral in virtue of the consecutive reaction symbolized: $2Na_2H_3IO_6+I_2=3NaIO_3+NaI+3H_2O$. According to E. Müller, in alkaline soln. with the substances concerned in normal soln., the electromotive force at platinized electrodes compared with the normal hydrogen electrode for the reaction: $KI+4H_2O\rightleftharpoons KIO_4+4H_2$, 0·387 volt; for $KI+3H_2O\rightleftharpoons KIO_3+3H_2$, 0·227 volt; and for $KIO_3+H_2O\rightleftharpoons KIO_4+H_2$, 0·513 volt. In a given system, says E. Müller, *a lower and a higher stage of oxidation can react only to form a given intermediate stage when all the reactions leading to the other intermediate compounds are accompanied by a loss of free energy*—*e.g.* the reaction between a periodate and iodide to form an iodate: $KI+3KIO_4=4KIO_3$. This reaction does not occur in alkaline soln., presumably because the interaction of these substances to form another intermediate substance say free iodine, is accompanied by a gain of energy. In acid soln., or in the presence of platinum black, in light, or at higher temp., this is no longer the case, and the reaction occurs: $KIO_4+2HI=I_2+KIO_3+H_2O$. The catalytic agent overcomes the passive resistance of the system. M. Bengieser stated that alcohol and ether are not decomposed by periodic acid, but, *au contraire*, C. Langlois said that almost all organic substances, including alcohol and ether, are slowly attacked.

Detection and determination.—The periodates behave towards reducing agents like the iodates. They are usually but slightly soluble in water and readily soluble in dil. nitric acid. When soln. of sodium periodate are added to barium, strontium, calcium, lead, and silver salts, precipitates of dimesoperiodates are obtained, and the mother liquor has an acid reaction—the silver salt is pale yellow, the others white—silver iodate is also white. The silver precipitate becomes dark red when boiled in water; the fresh precipitate is very soluble in ammonia, the dark red

precipitate is sparingly soluble. Tannic acid precipitates a periodate from soln. of periodic acid but not from iodic acid—the precipitate is soluble in ammonia or potash lye and the soln. becomes dark red on exposure to air. Gallic acid does not give a precipitate, but only a coloured soln. Periodic acid and the periodates can be determined by adding potassium iodide and dil. sulphuric acid and titrating the separated iodine; by their action on oxalic acid in the presence of manganese sulphate, and determining the liberated iodine; by treatment with hydrogen peroxide and measuring the oxygen evolved.

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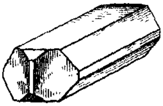
§ 17. The Perchlorates

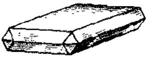
The perchlorates are prepared by the action of the acid on a suitable base, by the thermal decomposition of certain chlorates, and by the electrolysis of chlorates. Perchloric acid is always monobasic: no acid salts have been made. Sodium perchlorate has been reported in the nitrates of Chili. According to M. H. Märker,[1] some specimens have up to 5·64 per cent. of this salt, and it has been suggested that the presence of perchlorates is the cause of the deleterious action of some deliveries of Chili saltpetre when used as a fertilizer for rye.

The alkali and ammonium perchlorates.—Lithium perchlorate was made by G. S. Sérullas by saturating perchloric acid with lithium hydroxide; A. Potilitzin[2] used the carbonate. The aq. soln. so obtained is evaporated to dryness and extracted with alcohol. The resulting crystals are anhydrous **lithium perchlorate,** $LiClO_4$. aq. soln. furnish **trihydrated lithium perchlorate,** $LiClO_4.3H_2O$, in hexagonal crystals. According to A. Potilitzin, the trihydrate at 100° forms **monohydrated lithium perchlorate,** $LiClO_4.H_2O$; and at 130°, the anhydrous salt. T. W. Richards and H. H. Willard prepared this salt in a high state of purity, and found it can be thoroughly dried by fusion: lithium chloride was dissolved in water, and treated with a slight excess of a constant boiling soln. of perchloric acid above that required for the conversion of the chloride to perchlorate. The mixture was evaporated to dryness under conditions where the mixture did not boil. The hydrochloric acid was soon expelled; the excess of perchloric acid was driven off by heat; and the temp. raised to the fusion point, when anhydrous lithium perchlorate was obtained in a high degree of purity: at a higher temp. it furnishes lithium chloride and oxygen: $LiClO_4=LiCl+2O_2$. Hence lithium perchlorate was used in some atomic weight determinations to find the ratio $LiCl:4O$. Sodium perchlorate was made by G. S. Sérullas by the action of perchloric acid on the hydroxide; by F. Penny by the action of nitric acid on the chlorate; and T. Schlösing by heating the chlorate. The electrolytic process is used on a large scale. A. Potilitzin showed that if the aq. soln. be crystallized above 50°, non-deliquescent prismatic crystals of anhydrous **sodium perchlorate,** $NaClO_4$, are formed, while if crystallized at room temp., or below 50°, deliquescent **monohydrated sodium perchlorate,** $NaClO_4.H_2O$, is formed. Either salt can be obtained by the seeding of a supersaturated soln. at room temp. with the proper salt. Anhydrous potassium perchlorate, $KClO_4$, was made by G. S. Sérullas, J. von Liebig, J. C. G. de Marignac, and others by processes analogous to those employed for the sodium salt. **Potassium perchlorate,** $KClO_4$, is also precipitated when perchloric acid or a soln. of sodium perchlorate is added to a soln. of a potassium salt—chloride, nitrate, acetate, etc. The excess of potassium salt is removed by washing with alcohol of sp. gr. 0·385; and the residual potassium perchlorate recrystallized from boiling water. Sparingly soluble **rubidium perchlorate,** $RbClO_4$, and **cæsium perchlorate,** $CsClO_4$, were obtained in a similar manner. E. Mitscherlich first

prepared crystals of **ammonium perchlorate,** *NH_4ClO_4, from barium perchlorate and* ammonium sulphate. T. Schlösing [3] treated hot soln. of sodium perchlorate with ammonium chloride, and on cooling crystals of ammonium perchlorate were obtained; U. Alvisi treated a mixture of 75·77 parts of ammonium nitrate and 213 of sodium perchlorate, and obtained a crop of small crystals of ammonium perchlorate which were purified by recrystallization from hot water; and C. W. Bailey, H. S. Denny, and A. J. Dunk, and O. B. Carlson patented the use of ammonium sulphate for this purpose. A. Miolati mixed magnesium or calcium perchlorate with ammonium chloride and crystals of ammonium perchlorate deposited from the soln. of very soluble magnesium or calcium chloride.

Crystals of lithium perchlorate are known only in the hydrated form, trihydrated lithium perchlorate, $LiClO_4.3H_2O$. The crystals belong to the hexagonal system with the axial ratio $a : c = 1·07039$, and J. W. Retgers [4] considers that they are probably isomorphous with trihydrated lithium permanganate, $LiMnO_4.3H_2O$. According to G. Wyrouboff the crystals have a negative double refraction, and according to A. Lagorio positive. The needle-like crystals of trihydrated sodium perchlorate, $NaClO_4.3H_2O$, are very like the corresponding lithium salt, but they are so hygroscopic that the crystalline form has not been determined. The anhydrous crystals of sodium perchlorate, $NaClO_4$, have not been measured. Potassium perchlorate forms rhombic bipyramidal crystals which, according to P. Groth, have the axial ratios $a : b : c = 0·7817 : 1 : 1·2792$. The crystals are usually prismatic, Fig. 30, but by the slow cooling of sat. soln., E. Mitscherlich obtained the form indicated in Fig. 31, and by the spontaneous evaporation of cold sat. soln.,





FIGS. 30 and 31.—Crystals of Potassium Perchlorate.

tabular crystals are obtained, Fig. 31. According to J. W. Retgers and T. V. Barker, potassium perchlorate forms an isomorphous series of mixed crystals with potassium permanganate. According to T. V. Barker, rubidium perchlorate, $RbClO_4$, crystallizes in thick plates belonging to the same system as the potassium salt, and possessing the axial ratios $a : b : c = 0·7966 : 1 : 1·2879$; while cæsium perchlorate, $CsClO_4$, likewise has the axial ratios $a : b : c = 0·7932 : 1 : 1·2808$; and ammonium perchlorate, NH_4ClO_4, has the axial ratios $a : b : c = 0·7932 : 1 : 1·2808$. E. Mitscherlich and P. Groth [5] also measured the crystal constants of ammonium perchlorate. All these salts are isomorphous with the corresponding permanganates.

The **specific gravity** of trihydrated lithium perchorate [6] is 1·841 according to G. Wyrouboff; while the sp. gr. of potassium perchlorate at 10·8° is 2·524 according to W. Muthmann, and at room temp., 2·520, according to H. G. F. Schröder; 2·525, according to T. V. Barker. The sp. gr. of rubidium perchlorate is 3·014; of cæsium perchlorate, 3·327; and of ammonium perchlorate, 1·952—all by T. V. Barker. F. W. Clarke gives for the last-named salt 1·89. According to M. M. P. Muir, the sp. gr. of an aq. soln. of potassium perchlorate, sat. at 0°, is 1·0005; at 25°, 1·0123; at 50°, 1·0181; and at 100°, 1·06603. B. Carlson has also measured the sp. gr. of aq. soln. of lithium, sodium, potassium, rubidium, cæsium, and ammonium perchlorates.

According to A. Potilitzin, the **melting point** of trihydrated lithium perchlorate is 95°; and, between 98° and 100°, the salt loses approximately two-thirds of its combined water; and all the water is lost between 130° and 150°; the anhydrous salt melts at 236°, and loses no oxygen at 300°; this gas is evolved at about 368°, at 380° the speed of decomposition is rapid—lithium chlorate and chloride are first

formed, and the speed of decomposition at 368° is greatest when the ratio $LiClO_4$: $LiClO_3$ is approximately 1 : 3. A. Potilitzin[7] found monohydrated sodium perchlorate becomes anhydrous at 130°. T. Carnelley and L. T. O'Shea give the m.p. of sodium perchlorate at 432°, and the salt slowly decomposes at this temp.; potassium perchlorate cannot be fused without comparatively rapid decomposition, but it is said to melt at about 610°, and to commence decomposing at 400°; according to F. L. Teed, it forms some chlorate during its decomposition. According to N. Louguinine, rubidium perchlorate easily melts when heated and decomposes at a dull red heat. Ammonium perchlorate, said P. G oth, is decomposed by heat into ammonium chloride, oxygen and chlorine; M. Berthelot[8] says into water, oxygen, nitrogen, and chlorine. During the concentration of an aq. soln. of ammonium perchlorate some ammonia is lost, and the soln. becomes acid. M. Berthelot gives for the **heat of formation** of sodium perchlorate, $NaClO_4$, from its elements, 100·2 Cals.; for potassium perchlorate, 112·5 Cals.; and for ammonium perchlorate, 79·7. The **heat of solution** of sodium perchlorate, in 200–400 mol. of water is 3·5 Cals. at 10°; for potassium perchlorate, −12·1 Cals.; and for ammonium perchlorate, −6·36 Cals. E. F. von Stackelberg found the heat of soln., Q, of a mol. of potassium perchlorate in 100 mol. of water to be $Q=12860-9200n$ cals. The **heat of neutralization** of perchloric acid with ammonia is 12·9 Cals. The **heats of the reactions** are given by $NaClO_4=NaCl+2O_2$ −3·0 Cals.; $NH_4ClO_4=Cl+O_2+N+2H_2O_{gas}$ +38·3 Cals. H. Kopp[9] found the **specific heat** of potassium perchlorate to be 0·190 between 14° and 45°.

M. M. P. Muir[10] has measured the **solubility** of potassium perchlorate; he found that at 0°, 100 grms. of water dissolved 0·71 grms. of potassium perchlorate; at 25°, 1·96 grms.; at 50°, 5·34 grms.; and at 100°, 18·7 grms. He also adds that "for each rise of 25° from 0° the solubility and the percentage amount of the salt in soln. increases in round numbers threefold." A. A. Noyes and co-workers found that 100 c.c. of water at 10° dissolved 1·082 grms. of potassium perchlorate; at 20°, 1·668 grms.; and at 30°, 2·494 grms. Determinations of the solubility of potassium perchlorate in water were also made by J. Hutstein, R. G. Thin and A. C. Cumming, B. Carlson, and G. S. Sérullas. According to W. Louguinine, 100 grms. of water at 2·13° dissolved 1·09 grms. of rubidium perchlorate, and 1·62 of the potassium salt. F. Calzolari noted that the solubility of cæsium perchlorate at 20° is a little less than that of the potassium salt; and greater than that of the rubidium salt—*vide* the solubility of the alkali chlorates. F. Calzolari's values for the solubilities of potassium, rubidium, and cæsium perchlorates in 100 grms. of water are:

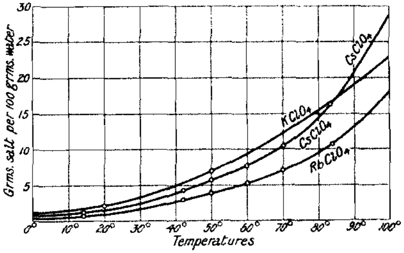


Fig. 32.—Solubilities of Potassium, Rubidium, and Cæsium Perchlorates in Water.

	8·5°	14°	33·7°	42°	50°	60°	70°	84°	99°
$KClO_4$	—	—	—	—	6·45	—	12·3	—	22·2
$RbClO_4$	0·59	0·767	1·84	2·64	3·55	4·85	6·72	10·42	17·39
$CsClO_4$	0·91	1·19	2·99	4·09	5·47	7·30	9·79	16·51	28·57

and these results are plotted in Fig. 32. B. Carlson found that at 15° and 50° water dissolves respectively 107·6 and 123·4 per cent. of sodium perchlorate when the

solid phase is $NaClO_4.H_2O$; and at 143°, 141·4 per cent. when the solid phase is $NaClO_4$. G. S. Sérullas found that 20 parts of ammonium perchlorate dissolved in 100 parts of cold water. R. G. Thin and A. C. Cumming found that water at 14·2° dissolves 1·735 per cent. of ammonium perchlorate. K. A. Hofmann, K. K. A. Höbold, and F. Quoos found 18·5 grms. of salt were dissolved by 100 grms. of water at 15°, and B. Carlson gave for the percentage solubility:

	0	20°	40°	60	80°	100	107°
NH_4ClO_4 . .	11·56	20·85	30·58	39·05	48·19	57·01	58·12
Sp. gr. . .	1·059	1·098	1·128	1·158	1·193	1·216	1·221

R. G. Thin and A. C. Cumming found that with aq. soln. of perchloric acid of normality *N*, water dissolves at 25·2°:

N	—	0·01	0·10	1·00
Per cent. $KClO_4$	2·085	1·999	1·485	0·527

A. A. Noyes and co-workers measured the depressed solubility of potassium perchlorate in aq. soln. of potassium chloride and potassium sulphate.

G. S. Sérullas says that lithium perchlorate is very soluble in alcohol; sodium perchlorate is soluble in the same menstruum; H. E. Roscoe says that potassium perchlorate is but very slightly soluble in absolute alcohol, and not at all if the alcohol contains a trace of an acetate. T. Schlösing reported that potassium chlorate is not soluble in alcohol of sp. gr. 0·835. According to R. G. Thin and A. C. Cumming, 100 grms. of 98·8, 93·5, and 51·2 per cent. soln. of ethyl alcohol dissolve, at 25·2°, respectively 0·019, 0·051, and 0·754 grms. of potassium perchlorate, and in the first two cases, if 0·2 per cent. of perchloric acid is present, respectively 0·028, and 0·0175 per cent. of that salt. G. S. Sérullas said ammonium perchlorate is slightly soluble in alcohol; P. Groth could find no sign of the formation of a basic salt when potassium perchlorate is treated with alkali lye. According to H. P. Pearson, potassium perchlorate dissolves more easily in soln. of ammonium nitrate than in water; and less easily in ammonium acetate, ammonium chloride, ammonia, or hydrochloric acid; dil. nitric acid dissolves about as much of this salt as does water and dil. acetic acid about half as much. According to V. Rothmund, aq. semi-normal soln. of the following menstrua dissolve, the indicated number of grams of potassium perchlorate per litre, at 25°: water alone, 20·44; *methyl alcohol*, 19·45; *ethyl alcohol*, 18·75; *propyl alcohol*, 18·61; *tertiary amyl alcohol*, 17·72; *acetone*, 20·11; *ether*, 18·51; *glycol*, 19·62; *glycerol*, 19·45; *urea*, 20·92; *ammonia*, 20·43; *dimethylamine*, 18·60; *pyridine*, 19·54; *urethane*, 19·40; *formamide*, 21·32; *acetamide*, 20·05; *acetic acid*, 20·26; *phenol*, 18·87; *methylal*, 19·40; *methyl acetate*, 19·80. F. Ephraim prepared **lithium tetrammino-perchlorate** as a solid which liquefies at ordinary temp.

G. Tammann [11] found the **vapour pressure** of water at 100° was lowered 7·8 mm. by the soln. of 5·06 grms. of potassium chlorate per 100 grms. of water; 17·4 mm. by 10·73 grms. of the salt; and 21·7 mm. by 13·64 grms. of the salt. The eq. **electrical conductivity** of lithium, sodium, and potassium perchlorates at 25° for a mol. of the salt in *v* litres of water are:

v	32	64	128	256	512	1024
$LiClO_4$ . . .	101·5	104·8	107·6	109·9	111·9	113·1
$NaClO_4$ . . .	111·4	114·9	117·7	120·0	121·6	123·7
$KClO_4$ . . .	131·9	135·9	140·3	143·5	145·8	146·4

H. C. Jones [12] also worked out the temp. coeff from 0° to 65°, and he gives for the ionization constants *a*:

v . .	8	32	128	512	1024	2048	4096
a $NaClO_4$.	84·5	93·0	98·5	100·0	99·7	—	—
a $KClO_4$.	—	86·9	93·0	95·9	97·1	98·5	100·0

R. Roth,[13] K. K. A. Höbold, A. G. von Zedtwitz, K. A. Hofmann and co-workers prepared a large number of perchlorates of the organic bases. K. A. Hofmann and

co-workers, and J. Milbauer also studied the properties of a number of organic perchlorates.

Cupric perchlorate.—G. S. Sérullas [14] prepared large blue deliquescent crystals by the evaporation of an aq. soln. of cupric oxide in perchloric acid. R. Roth's analyses of the crystals of cupric perchlorate gave $Cu(ClO_4)_2.6H_2O$ or, by A. Werner's theory, $[Cu(H_2O)_6](ClO_4)_2$. Paper soaked in the soln., dried, and placed on red-hot coals burns with a greenish-blue flash. H. E. Roscoe prepared a sparingly soluble dehydrated **cupric hexammino-diaquo-perchlorate,** $Cu(ClO_4)_2.4NH_3.2H_2O$—or, according to A. Werner's theory, $[Cu(H_2O)_2(NH_3)_4](ClO_4)_2$. P. Sabatier found soln. of cupric perchlorate formed a basic perchlorate, $Cu(ClO_4)_2.4CuO$, when treated with the partially dehydrated brown cupric hydroxide

Silver perchlorate, $AgClO_4$, was made by G. S. Sérullas (1831) [15] by the evaporation of a soln. of silver oxide in perchloric acid; and by P. Groth (1868) by double decomposition with barium perchlorate and silver sulphate. T. Carnelley and L. T. O'Shea give the m.p. as 486°, and it decomposes suddenly just below a red-heat. G. Bruni and G. Levi give $-2·17$ Cals. for the heat of soln. of a mol. in 1600 mols. of water. According to W. Nernst and M. Löb, the electrical conductivity, λ, of soln. with 0·025 mol. per litre is 0·0001109; and 0·0001200 in soln. with 0·0008 mol. per litre. G. Gore found that during the electrolysis of aq. soln. of silver chlorate the anode was covered with a black film—probably silver peroxide. Aq. soln. become brown on exposure to light. Soln. in aq. ammonia furnish a crystalline **silver diammino-perchlorate,** $AgClO_4.2NH_3$, whose heat of formation in the solid state, according to G. Bruni and G. Levi, is $AgClO_4 + 2NH_3 = 38·40$ Cals.; heat of formation in soln. is $AgClO_{4aq.} + 2NH_{3aq.} = 12·71$ Cals.; and whose molecular heat of soln. in 1600 mols. of water is $-10·71$ Cals. These results are taken to show that only the diammino-salts exist in soln. The heat of formation of **silver triammino-perchlorate** is $AgClO_4 + 3NH_3 = AgClO_4.3NH_3 + 47·77$ Cals. The solid triammino-salt is immediately decomposed into the diammino-salt and ammonia when dissolved in water. They also made **dimethylammino-silver perchlorate,** $AgClO_4.2NH_2CH_3$.

The perchlorates of the alkaline earths.—G. S. Sérullas [16] prepared deliquescent prisms of **calcium perchlorate** in 1831. The alcoholic soln. burnt with a red flame; **strontium perchlorate,** with a purple flame. G. S. Sérullas made **trihydrated barium perchlorate,** $Ba(ClO_4)_2.3H_2O$, in hexagonal crystals, by the action of the acid on the hydroxide or carbonate; P. Groth made it by the action of potassium perchlorate on hydrofluosilicic acid, and, after washing the potassium fluosilicate, neutralizing the liquid with barium carbonate. This soln. was evaporated to dryness, and barium perchlorate was extracted from the residue by alcohol; and any barium chloride present was removed by treatment with silver perchlorate. O. Henry boiled zinc fluosilicate with an aq. soln. of potassium chlorate, and treated the soln. of zinc perchlorate with baryta water—zinc hydroxide was precipitated; barium perchlorate remained in soln.

J. Grossmann prepared barium perchlorate on a manufacturing scale by evaporating a mixed soln. of sodium perchlorate and barium chloride. Crystals of sodium chloride crystallize out before the barium perchlorate. F. Winteler made the salt by the electrolysis of barium chloride. According to J. C. G. de Marignac, the hexagonal crystals have the axial ratio $a : c = 1 : 0·6623$. According to G. Wyrouboff, the crystals have a feeble negative double refraction. J. C. G. de Marignac's analysis make the composition of the salt $Ba(ClO_4)_2.4H_2O$; but G. S. Sérullas' result: $Ba(ClO_4)_2.3H_2O$, is usually considered to have been correct. Two-thirds of the combined water is lost over conc. sulphuric acid; the remaining third at 100°. A. Potilitzin says the salt begins to decompose at 400° when 0·09 per cent. of oxygen was lost in 70 minutes; at 460° all the oxygen was lost in about 9½ hours. According to T. Carnelley and L. T. O'Shea, barium perchlorate melts at 505°. The salt is very soluble in water and alcohol. Paper, soaked in the soln. and dried, burns with a green flame.

The perchlorates of beryllium, magnesium, zinc, cadmium, and mercury.—A. Atterberg,[17] and J. C. G. de Marignac prepared **tetrahydrated beryllium perchlorate,** $Be(ClO_4)_2.4H_2O$, in deliquescent needle-like crystals after conc. of the soln. to a thick syrup. The crystals give off vapour of perchloric acid at 100°, and form beryllium oxide on calcination. G. S. Sérullas prepared long prisms of deliquescent crystals of **magnesium perchlorate**; and likewise of **zinc perchlorate** by evaporating the soln. obtained by the double decomposition of the metal sulphate and barium perchlorate. The crystals are deliquescent, and soluble in alcohol. G. S. Sérullas also made similar crystals of **cadmium perchlorate** by evaporating the soln. of the oxide in perchloric acid.

G. S. Sérullas[18] (1831) and H. E. Roscoe made **mercurous perchlorate,** $HgClO_4.2H_2O$ or $HgClO_4.3H_2O$, by the action of the acid on mercurous oxide. The soln. is conc. on a water-bath, and crystallized in a desiccator. According to M. Chikashigé, a soln. of mercurous perchlorate is also formed by shaking for about 4 hrs. a soln. of mercuric chlorate with mercury—the product, says F. Teltscher, still contains about 1·4 per cent. of mercuric perchlorate. The needle-like crystals are stable in dry air, deliquescent in moist air. They lose very little in vacuo, or at 100°—a specimen lost about 6 per cent. of water when kept two weeks in a vacuum desiccator; and 2 per cent. when heated 6 hrs. in a stream of air at 100°. When heated to 100°, the salt decrepitates and remains completely soluble in a little water; at 150°, the crystals lose some acid, they swell slowly, and become opaque in consequence of the formation of what appears to be a basic salt, mercuric perchlorate, and a trace of mercuric chloride; at 170°, more of the basic salt and of the mercuric salts are formed, and some chlorate; and at 200°, the mercuric chloride begins to sublime. The more the salt is heated, the more basic it becomes, and the greater the residue remaining when it is extracted with water, and the less mercurous nitrate it forms when treated with nitric acid. Mercurous perchlorate is very deliquescent, but less so than the mercuric salt; it is very soluble in water, forming a soln. neutral to litmus. The eq. electrical conductivity, λ, in reciprocal ohms at 25°, is 109·9 for a mol. of the salt in 10 litres, and 175·9 for a mol. in 1024 litres. H. Ley found the electromotive force of the cell Hg | HgCl; $\frac{1}{10}N$-KCl; $\frac{1}{10}N$-$HgClO_4$ | Hg at 20° to be 0·4193 volt; and for normal NaCl, 0·4719 volt. G. A. Linhart also measured the potential of mercurous perchlorate soln. against a mercury electrode. The potential of the soln. against a smooth platinum electrode is not sensitive to light; if perchlorate acid be present, the result is different. Mercurous perchlorate is slowly hydrolyzed by an excess of water, or when the soln. is heated for a long time on a water-bath, and a basic salt is formed. The degree of hydrolysis for $\frac{1}{10}N$-soln. is 0·034. The white basic salt formed by hydrolysis is blackened when washed with water. Alcohol decomposes the solid salt into a soluble and white insoluble basic salt which is blackened if washed with water, but not with alcohol. Alcohol does not effect aq. soln.; but they are blackened by ammonia. The needle-like crystals, which M. Chikashigé obtained by concentrating the alcoholic soln. of mercurous perchlorate, appear to be a mixture of $HgClO_4 : Hg(ClO_4)_2 = 20 : 1$.

G. S. Sérullas (1831)[19] and H. E. Roscoe (1866) obtained crystals of **hexahydrated mercuric perchlorate,** $Hg(ClO_4)_2.6H_2O$, by saturating an aq. soln. of perchloric acid with mercuric oxide, and concentrating the soln. by evaporation. M. Chikashigé made the same crystals rubbing up mercuric oxide with perchloric acid until the soln. begins to appear turbid; it is then filtered through asbestos, mixed with a few drops of perchloric acid, evaporated at a gentle heat, and finally evaporated at ordinary temp. over sulphuric acid. The mother liquid is removed from the crystals by suction; and the crystals dried on a porous tile. The prismatic crystals are difficult to dry; they effloresce slowly in a desiccator, and deliquesce rapidly in air; and melt with a slight rise of temp.—34° in dry air. The aq. soln. reddens litmus, and M. Chikashigé says that the soln. contains no free acid because the soln. becomes neutral when an excess of sodium chloride is added to

the soln. This, of course, is wrong. The salt is no doubt hydrolyzed into free acid, etc., and the sodium chloride presumably either drives back the hydrolysis or forms a more stable double salt. The soln. decomposes when evaporated by the aid of heat, to form an insoluble basic salt. The solid effloresces in a desiccator owing to the loss of acid and water with the formation of an insoluble basic salt. The decomposition is accelerated by exposure to light. When heated to 120°, water and perchloric acid appear in the issuing vapour ; if it be heated gradually to 150°, and maintained at that temp. to a constant weight, the **basic mercuric perchlorate,** $2HgO.Hg(ClO_4)_2$, is formed as a white amorphous precipitate which is not changed at the b.p. of mercury, and only slightly attacked at the b.p. of sulphur. This basic salt is hydrolyzed by water into mercuric perchlorate and mercuric oxide with a little mercuric chloride and chlorate. According to H. Ley, the eq. conductivity, λ, of hexahydrated mercuric perchlorate at 25° is 119·3 with a gram-eq. per 32 litres ; and 232·7 with a gram-eq. in 512 litres of water. The potential of the soln. against a smooth platinum electrode becomes positive when exposed to light, and this the more in the presence of perchloric acid. Alcohol decomposes the salt very quickly, leaving a white insoluble basic salt, which is decomposed by water to form mercuric oxide. The addition of alcohol to an aq. soln. of the salt gives an orange precipitate which is mainly mercuric oxide. M. Chikashigé says that on evaporating the mother liquor there is very little reduction to mercurous state, and what there is is probably due to the reduction of mercuric salts by hot alcohol. Alcoholic soln. decompose more readily than aq. Prismatic crystals of the **basic mercuric perchlorate,** $HgO.2Hg(ClO_4)_2.12H_2O$, were made by M. Chikashigé by digesting perchloric acid with an excess of mercuric oxide, and after filtering the soln. through asbestos, concentrating first on a water-bath, and then in a desiccator, drying the crystals on a porous tile. If these crystals be boiled with alcohol, a white flocculent precipitate of the anhydrous salt is obtained, insoluble in hydrochloric or nitric acid, but decomposed and dissolved by aqua regia. The anhydrous salt is stable up to a dark-red heat, it then detonates vigorously.

A. G. von Zedtwitz prepared **nitrosyl perchlorate,** $NOClO_4.H_2O$, by evaporating commercial 20 per cent. perchloric acid in a porcelain dish until the temp. reached 140°, and thick white vapours appeared. The product, $HClO_4.2H_2O$, was treated with a gaseous mixture of nitric oxide and nitrogen peroxide evolved from a mixture of 68 per cent. nitric acid with sodium nitrite either at ordinary temp. or at 0°. Colourless plates separate out in such quantities that the whole liquid seems to solidify. Hence, precautions must be taken against the choking of the gas delivery tube. The crystals are separated by suction on a Gooch's platinum crucible, dried over phosphorus pentoxide in an atmosphere of nitric oxide and nitrogen peroxide, and finally in vacuo. After standing eight days over phosphorus pentoxide and vacuo some water is lost but no nitric oxide. It is not split into nitric oxide and in chlorine oxide when heated to 110°, but the perchloric acid is completely decomposed, and the constitution of the product is supposed to be $ClO_3-O-NO+H_2O$. It is slightly hygroscopic, and gradually decomposes in moist air. With phosphorus pentoxide, it forms a brown mass of syrupy consistency—perchloric acid under similar conditions may explode. Sulphuric acid forms an analogous product. R. Roth prepared **antimony perchlorate** by warming antimony trioxide in hot 60–70 per cent. perchloric acid. As the soln. cools the salt separates out. Arsenic trioxide under similar conditions furnishes the unchanged oxide. M. M. P. Muir [20] prepared a **bismuthyl perchlorate,** $BiO.ClO_4$, or *basic bismuth perchlorate,* $Bi_2O_3.Bi(ClO_4)_3$, as a white mass by heating metallic bismuth with an aq. soln. of perchloric acid. The salt is " almost perfectly " insoluble in water at 100° ; it is readily dissolved by hydrochloric or nitric acid ; and less readily by sulphuric acid. It is decomposed at a red heat, when bismuth chloride is slowly formed and volatilized.

G. S. Sérullas [21] prepared a crystalline mass of **aluminium perchlorate** by evaporating a soln. of aluminium hydroxide in perchloric acid. The crystals are

deliquescent, redden litmus, and dissolve in alcohol. According to D. H. Dobroserdoff, the rapid decomposition of hexahydrated aluminium chlorate by heat gives a residue containing the eq. of $Al_2O_3 + 2Al(ClO_4)_3$. W. Crookes reports that aq. perchloric acid easily dissolves scandium hydroxide or carbonate, and, when the soln. is evaporated over the water-bath, a felt-like mass of rhombic needle-shaped crystals of **scandium perchlorate** separate. **Yttrium perchlorate,** $Y(ClO_4)_3.9H_2O$, was prepared by P. T. Cleve [22] in hygroscopic needle-like crystals by the double decomposition of yttrium sulphate and barium perchlorate. Deliquescent needles of **lanthanum perchlorate,** $La(ClO_4)_3.9H_2O$, and **didymium perchlorate,** $Di(ClO_4)_3.9H_2O$, were also made by P. T. Cleve in a similar manner. These salts are deliquescent, and soluble in alcohol.

F. C. Mathers and C. G. Schlüderberg [23] made colourless deliquescent crystals of **indium perchlorate,** $In(ClO_4)_3.8H_2O$, by dissolving electro-deposited indium (previously fused in a charcoal crucible in a stream of hydrogen) in perchloric acid. The soln. was evaporated on a hot plate until it deposited small crystals when cooled by a mixture of ice and salt. Further evaporation was conducted under reduced press. over sulphuric acid. The crystals were rapidly rinsed with a small amount of water, and dried on filter paper. The compound is soluble in water and absolute alcohol, but less soluble in ether. Basic salts, the products of hydrolysis, are precipitated from a neutral soln. at 40°. The crystals fuse at about 80° in air, and they decompose at a higher temp. below a red heat. Rhombic crystals of **thallous perchlorate** were made by W. Crookes in 1863 by the soln. of the metal in the perchloric acid; by the action of barium perchlorate on thallous sulphate; and by J. W. Retgers by the action of perchloric acid on thallous carbonate. W. Crookes also described what he regarded as **thallic perchlorate** with $1·5H_2O$. Thallous perchlorate is more readily soluble than rubidium or cæsium perchlorates; according to H. E. Roscoe, 100 grms. of water at 15° dissolve 10 grms. of the salt, and at 100°, 116·7 grms. of the salt. It is insoluble in alcohol. According to H. E. Roscoe, the salt decomposes about the b.p. of mercury, blackens, and volatilizes as thallous chloride. T. Carnelley and L. T. O'Shea give the m.p. at 510°. According to E. Franke, at 25° the eq. conductivity of a soln. containing a mol. of the salt in 32 litres of water is 129·3; and in 1024 litres, 143·7.

Lead oxide or carbonate dissolves in perchloric acid,[24] forming a soln. from which crystals of **lead perchlorate,** $Pb(ClO_4)_3.2H_2O$, can be obtained in readily soluble white needle-like crystals; while H. E. Roscoe's analysis corresponds with "$3H_2O$," J. C. G. de Marignac's and R. Roth's analyses correspond with "$2H_2O$." At 100° the salt decomposes, giving off so much perchloric acid that paper held over the dish is carbonized. When the aq. soln. of lead perchlorate is boiled with an excess of lead carbonate and water, a **basic lead perchlorate**, $Pb(ClO_4)_2.Pb(OH)_2.H_2O$, *i.e.* $Pb(ClO_4)OH.\frac{1}{2}H_2O$, is formed in two different types of monoclinic crystals. S. Jolin prepared deliquescent plates of **cerous perchlorate,** $Ce(ClO_4)_3.H_2O$, by crystallization of the clear liquid obtained by treating cerous sulphate with barium perchlorate. S. Jolin and G. T. Morgan and E. Cahen prepared **cerium perchlorate,** $Ce(ClO_4)_3.9H_2O$, as a deliquescent crystalline mass from barium perchlorate and cerium sulphate. The water of crystallization is not all eliminated at 160°. F. Terlikowsky prepared **praseodymium perchlorate** and **neodymium perchlorate** by dissolving the respective carbonates in perchloric acid, and removing the excess of acid at 110°. Cubic crystals, *en tremis*, are obtained by evaporation in vacuo. The salts are less readily soluble in absolute alcohol than the perchlorates of cobalt, nickel, or chromium. The index of refraction is 1·50.

P. T. Cleve obtained an amorphous mass—presumably of **thorium perchlorate**—by treating thorium sulphate in a similar way. F. P. Venable and I. W. Smithey prepared **zirconyl perchlorate** by dissolving zirconium hydroxide in 30 per cent. perchloric acid; with 60 per cent. acid, the hydroxide dissolves

very slowly. After the acid had stood some weeks in contact with an excess of hydroxide, the clear decanted liquid was evaporated over calcium chloride, when crystals of $4ZrO(ClO_4)_2.HClO_4$ were obtained. The normal perchlorate was not obtained owing to hydrolysis. The salt $4ZrO(ClO_4)_2.HClO_4$ can be dissolved in water and recrystallized without further change. Two mol. of the salt in soln. can dissolve two mol. of zirconium hydroxide, forming $ZrO(OH)_2.9ZrO(ClO_4)_2$, which is also crystalline. When this salt is dissolved in water it furnishes the more stable salt, $4ZrO(ClO_4)_2.HClO_4$. The radiating clusters of crystals of the less stable form were also obtained by heating perchloric acid with an excess of zirconium hydroxide on a water-bath, and cooling the sat. soln. The crystals were washed with a little water. They are very deliquescent, odourless, soluble in alcohol, ether, benzene, chloroform, and carbon tetrachloride, but no crystals were obtained from these soln. The crystals begin to decompose below 100°, and when slowly heated they intumesce and give finally a white mass of zirconia; if suddenly heated they may explode with a sharp report.

G. S. Sérullas[25] prepared deliquescent needle-like crystals of **manganous perchlorate** by an analogous process. The crystals are soluble in absolute alcohol. R. Roth's analysis of the pale rose-coloured crystals corresponds with $Mn(ClO_4)_2.6H_2O$. F. Sabot has prepared hexagonal crystals of **chromic perchlorate.** F. Terlikowsky obtained the same salt by dissolving the hydroxide in perchloric acid and evaporating the soln. under reduced press. over sulphuric acid. The pale brownish-green crystals have a mean index of refraction 1·55, and they are slightly polychroïc. R. Roth's analysis of the crystals corresponds with $Cr(ClO_4)_3.6H_2O$. When heated the crystals become green, and melt at 94°. At 109° (toluene bath), the salt loses water and perchloric acid; and at 210°, it forms chromyl chloride and chromic acid. The crystals are very deliquescent, the aq. soln. is violet, and on boiling the soln. becomes green. When the hot green soln. is slowly cooled, the violet colour is restored. R. Roth failed to get green crystals from the green soln. cooled rapidly to a low temp.—the violet form was always produced. The cause of the colour changes is analogous with those which occur with the chloride. The alcoholic soln. retains its green colour longer than the aq. soln. C. F. Rammelsberg tried to make **uranyl perchlorate** by dissolving uranium hydroxide in perchloric acid, but when the attempt is made to crystallize the soln. by evaporation over conc. sulphuric acid, the product decomposes into uranyl chloride.

G. S. Sérullas also prepared crystals of **ferrous perchlorate,** $Fe(ClO_4)_2.6H_2O$, in an analogous manner, and H. E. Roscoe obtained the same salt by the action of iron on perchloric acid. The green crystals are very deliquescent. The water is not expelled at 100°, and the salt decomposes at a higher temp. The soln. of ferrous perchlorate gradually deposits a **basic ferric perchlorate** on exposure to air. A soln. of **ferric perchlorate,** $Fe(ClO_4)_3$, is obtained by dissolving hydrated ferric hydroxide in perchloric acid; R. Roth prepared very deliquescent almost colourless crystals of the salt which have the composition $Fe(ClO_4)_3.9H_2O$, and which dissolve in water, forming an intense yellowish-red liquid. The colour of the crystals darkens at about 75°, and at 210° they decompose. Indeed, almost all the inorganic perchlorates with water of crystallization decompose readily at 210°, which is approximately the b.p. of dihydrated perchloric acid. P. Groth prepared crystals of the **nickel perchlorate** by double decomposition of the sulphate with barium perchlorate; and P. Groth, F. Terlikowsky, and R. Roth prepared the salt by the crystallization from a soln. of the hydroxide or carbonate in the acid. The bluish-green prismatic crystals have a composition corresponding with $Ni(ClO_4)_2.6H_2O$; but if dried over sulphuric acid, in vacuo, F. Terlikowsky gives $Ni(ClO_4)_2.5H_2O$; they are feebly polychroïc, and belong to the hexagonal system. The index of refraction is 1·55. The crystals are very deliquescent, and can be dried by heating them in a current of dry air, or by confining them under reduced press. over sulphuric acid. The m.p. is 149°. The solubility, *S*, expressed in terms

of the number of mols of the anhydrous perchlorate in 100 mols of water, and the sp. gr. of the soln. are, according to F. Terlikowsky :

	−30·7°	−21·3°	0°	7·5°	18°	26°	45°
S	6·2887	6·4314	7·3048	7·4585	7·6901	7·8340	8·2765
Sp. gr.	—	—	1·5726	1·5755	1·5760	1·5841	1·5936

They are soluble in alcohol; but if the salt has been heated over 103°, the product does not dissolve entirely in water or alcohol—possibly owing to the formation of a basic salt or to decomposition—the yellow insoluble residue is soluble in nitric acid. R. Roth treated an ammoniacal soln. of a nickel salt with ammonium perchlorate and obtained pale blue octahedral crystals of a sparingly soluble salt, which, when recrystallized from ammonia water, have the composition of **nickelous hexammino-perchlorate,** $Ni(NH_3)_6(ClO_4)_2$. When heated, the salt detonates like ammonium perchlorate. **Cobalt perchlorate** is prepared in an analogous manner by dissolving the hydroxide in perchloric acid. According to R. Roth's observations, the rose-red octahedral crystals have the composition $Co(ClO_4)_2.6H_2O$, and they are rather more deliquescent than the corresponding nickel salt. F. Terlikowsky represented the composition of the pale rose-red hexagonal crystals dried over sulphuric acid by: $Co(ClO_4)_2.5H_2O$; and he found they were feebly polychroïc. The index of refraction is 1·55; the m.p. of the crystals is 143°, and they do not decompose at 103°. The salt is very soluble in water, acetone, and alcohol, but insoluble in chloroform. The sp. gr. of the aq. soln., and the solubility, *S*, expressed as in mols of the anhydrous perchlorate per 100 mols of water, are :

	−30·7°	−21·3°	0°	7·5°	18°	26°	45°
S	5·6536	6·3211	6·9983	7·1123	7·2444	7·9178	8·0328
Sp. gr.	—	—	1·5639	1·5658	1·5670	1·5811	1·5878

Octahedral rose-red crystals of **cobaltous hexammino-perchlorate,** $[Co(NH_3)_6](ClO_4)_2$, were prepared by R. Roth in a similar manner to the nickelous salt. U. Alvisi [26] has prepared some *luteocobalti ammonium perchlorates*, namely, golden-yellow cubic crystals of **cobaltic hexammino-perchlorate,** $[Co(NH_3)_6](ClO_4)_3$, and golden-yellow trigonal crystals of **cobaltic hexammino-diperchlorato-chloride,** $[Co(NH_3)_6](ClO_4)_2Cl$, with the axial ratio $a : c = 1 : 1·9300$, $\alpha = 71° 20'$. The former is obtained by heating aq. cobalt perchlorate with an excess of ammonium perchlorate and ammonia, and adding sodium or potassium permanganate until the liquid assumes a golden-yellow colour; or by heating a soln. of cobalt perchlorate with lead dioxide, ammonia, and an excess of ammonium perchlorate until the filtered liquid becomes intensely orange-yellow. R. Roth made crystals of $[Co(NH_3)_6](ClO_4)_3$, by treating a soln. of luteocobaltic chloride with perchloric acid. The aq. soln. when conc. gives golden-yellow octahedra. The crystals detonate when heated. When the soln. is treated with hydrochloric acid it yields crystals of the diperchlorate-chloride; and the same salt is formed in golden-yellow hexagonal plates by the interaction of cold sat. soln. of ammonium perchlorate and luteo-cobaltiammine chloride. This salt explodes when rapidly heated to 188°. By analogy with the hexammino-salts, the hexahydrated chromic, manganous, nickelous, cobaltous, and cupric perchlorates are supposed to be hexaquo-salts, $[Co(H_2O)_6](ClO_4)_2$, and $[Cu(H_2O)_6](ClO_4)_2$, while H. E. Roscoe's cupric salt is supposed to be cupric hexammino-diaquo-perchlorate, $[Cu(NH_3)_4(H_2O)_2](ClO_4)_2$. Hydrated ferric perchlorate is likewise regarded as $[Fe(H_2O)_6](ClO_4.H_2O)_3$. A number of organic perchlorates have been prepared by K. K. A. Höbold,[27] R. Roth, and A. G. von Zedtwitz.

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§ 18. Periodates

Although the periodates can be conveniently named in accord with the system indicated in Table III, decisive evidence is usually wanting to show whether some salts are hydrated forms of the salt of one acid, or acid salts of another acid. For example, it is not at all clear whether the periodate, $2Na_2O.I_2O_7.3H_2O$, is *secondary sodium paraperiodate*, $Na_2H_3IO_6$, or trihydrated *sodium dimeso-periodate*, $Na_4I_2O_9.3H_2O$. In addition to the periodates, of the various periodic acids there are a number of complex salts and acids, typified by the *hexamolybdato-periodates*, $5M_2O.I_2O_7.12MoO_3$; the *tetramolybdato-periodates*, $4M_2O.I_2O_7.8MoO_3$, and the *monomolybdate-periodates*, $3M_2O.I_2O_7.2MoO_3$, where M represents a univalent alkali metal. Tungsten as well as molybdenum salts are known. There are many analogies [1] between periodic acid and periodates on the one hand, and telluric acid and the tellurates on the other. The solubilities of the alkali salts in both cases decrease in passing from the cæsium salts to the very sparingly soluble sodium salts. The highly basic Ag_6TeO_6 and Ag_5IO_6 are prepared in a similar way. Both acids form complex ions, $[TeO_6]^{VI}$ and $[IO_6]^{V}$, respectively, and there are analogous $M_6[Te(MoO_4)_6]$ and $M_5[I(MoO_4)_6]$, and $M_6[Te(WO_4)_6]$ and $M_5[I(WO_4)_6]$. This is connected with the fact that the tendency of the acids to associate into complexes increases in the vertical series of the periodic table up to the formation of partly colloidal acids as occurs with the neighbours of iodine—tin (W. Mecklenburg), antimony (G. Jander), and tellurium (A. Rosenheim and G. Jander)—in the same horizontal series.

The periodates of the alkali metals and ammonium.—C. F. Rammelsberg [2] prepared white tetragonal crystals of **lithium metaperiodate,** $LiIO_4$, from a soln. of lithium dimesoperiodate in periodic acid crystals. The crystals are isomorphous with the corresponding ammonium, sodium, and silver salts. The

axial ratio is $a:c=1:1\cdot5272$. The crystals are slightly soluble in water, and the soln. has an acid reaction. When a dil. soln. of periodic acid is neutralized with dil. sodium hydroxide, a soln. of what is supposed to be sodium metaperiodate is formed. Sodium dimesoperiodate dissolves in periodic acid with the separation of colourless tetragonal crystals of **sodium metaperiodate,** which, according to T. V. Barker, are isomorphous with the periodates of ammonium, lithium, and silver. The crystals readily dissolve in water, forming an acid soln. The solid salt loses very little in weight when calcined at 190°; at 300° it changes to the iodate, and at higher temp. into the iodide. According to T. V. Barker, the crystals of anhydrous sodium metaperiodate are isomorphous with the corresponding ammonium, potassium, and rubidium salts. Its sp. gr. at 16° is 3·865 (water at 4° unity); and the mol. vol. is 55·37. The raising of the b.p. of water, determined by O. Liebknecht, is 0·108 for soln. of 4·50 grms. in 100 grms. of water, and 0·702° for soln. with 16·88 grms. of the salt in 100 grms. of water. From this it is inferred that the mol. wt. of the salt in soln. ranges from 125 to 130, corresponding with the ionization of two-thirds of the dissolved salt assumed to be the normal periodate. Crystals of **dihydrated sodium metaperiodate**, $NaIO_4.2H_2O$, or, according to P. Walden, *primary sodium paraperiodate*, NaH_4IO_6, separate from the acid soln. between 50° and 60°, and lose about 14·5 per cent. of water between 140° and 150°. Nitric acid soln. of sodium dimesoperiodate furnish trigonal, tetartohedral or hemihedral crystals of **trihydrated sodium metaperiodate,** $NaIO_4.3H_2O$, with $a:c=1:1\cdot0942$, and $\alpha=94°\ 8'$. The sp. gr. is 3·219 at 18° (water at 4° unity); and the mol. vol. is 83·28. The double refraction is feebly positive. P. Groth gives a rotation of the plane of polarization of 23·3° for the *D*-line, for plates a millimetre thick and 47·1° for the *G*-line. According to W. G. Hankel and H. Lindenberg, the crystals show piezo- and pyro-electrical phenomena. The crystals exhibit right- and left-handed circular polarization. If the mother liquid contains a great excess of sodium nitrite, says A. S. Eakle, the left-handed form preponderates. The crystals are isomorphous with ammonium periodate. The aq. soln. reacts acid. The crystals effloresce in air, and lose water rapidly; they become anhydrous over conc. sulphuric acid. At 200°, the crystals lose 18·68 per cent. of water; at 300°, they form sodium iodate; and the residue is neutral and free from iodide. The aq. soln. reddens on exposure to air and forms the iodate. According to E. Péchard, sodium iodide reacts with soln. of the metaperiodate: $3NaIO_4+2NaI+3H_2O=NaIO_3+2Na_2H_3IO_6+I_2$, followed by the secondary reaction: $2Na_2H_3IO_6+I_2=3NaIO_3+NaI+3H_2O$.

Normal potassium periodate, *i.e.* **potassium metaperiodate,** KIO_4, was prepared by A. Ihre,[3] by the oxidizing action of chlorine on a hot soln. of potassium iodate and hydroxide, with the latter in excess. According to C. F. Rammelsberg, it forms rhombic crystals isomorphous with potassium perchlorate, but, according to T. V. Barker, C. F. Rammelsberg mistook a specimen of potassium perchlorate for the periodate; and the periodate forms tetragonal bipyramids. No rhombic form is known. The sp. gr. of the salt is 3·618 at 13° (water at 4° unity), the mol. vol. is 63·60. 100 grms. of water dissolve 0·66 grm. of the salt at 13° and the soln. has an acid reaction. The sp. gr. of the sat. soln. at 13° is 1·0051. According to C. F. Rammelsberg, the solid does not change at 200°, but at 300° it loses oxygen and forms the iodate; and when calcined at a higher temp. it forms the iodide. T. Carnelley and W. C. Williams say the solid decrepitates at 389° and melts at 582°. J. Philipp states that chlorine—hot or cold—has no action on a soln. of potassium metaperiodate; iodine has no action on the boiling soln., but is oxidized to iodic acid at 160°, and the periodate forms the iodate, KIO_3. A soln. of potassium metaperiodate dissolves iodine forming a colourless soln. of iodate. Potassium iodide also forms iodate, without the separation of iodine: $3KIO_4+KI=4KIO_3$.

T. V. Barker[4] prepared **rubidium metaperiodate,** $RbIO_4$, by a method similar to that employed for the potassium compound, and the colourless tetragonal

crystals are strictly isomorphous with potassium metaperiodate. The sp. gr. at 16° is 3·918 (water at 4° unity); the mol. vol. is 70·56. 100 parts of water at 13° dissolve 0·65 parts of the salt, and the sp. gr. of the sat. soln. at 16° is 1·0052. The *chlorine oxidation process does not give a good yield of cæsium metaperiodate, for* a great proportion is precipitated as iodate. H. L. Wells' process gives better results. He prepared *normal cæsium periodate, that is,* **cæsium metaperiodate,** $CsIO_4$, crystallizing in well-defined rhombic plates which are not isomorphous with the corresponding compounds of rubidium and potassium. The crystals of cæsium metaperiodate have a sp. gr. of 4·259 (water at 4° unity); and the mol. vol. is 76·04. 100 grms. of water at 15° dissolve 2·15 parts of the salt, so that the salt is relatively soluble in water. It can be readily recrystallized from hot water. The sp. gr. of a sat. soln. at 15° is 1·0166. The acid salt, **acid cæsium iodatoperiodate**, $CsIO_4.HIO_3$, or $HCs(IO_3)IO_4$, crystallizes in soluble prismatic crystals from a soln. of cæsium periodate in dil. periodic acid, in which the periodic acid has suffered a little reduction; or from a soln. of cæsium iodate and periodate in periodic acid.

C. F. Rammelsberg and T. V. Barker made anhydrous **ammonium metaperiodate,** NH_4IO_4, in tetragonal crystals which are isomorphous with the corresponding sodium, potassium, and rubidium salts, and which have the axial ratio $a:c=1:1·5211$. The sp. gr. of the salt at 18° is 3·056 (water at 4° unity); and the mol. vol. is 68·39. The *salt is soluble in water,* 100 grms. of water at 16° dissolve 2·7 grms. of the salt, and the sp. gr. of the sat. soln. at 16° is 1·0178. The aq. soln. has an acid reaction. When *heated, ammonium metaperiodate detonates, forming iodine, oxygen, nitrogen,* ammonia, and water. A. Ihre prepared crystals of what he regarded as **trihydrated ammonium periodate,** $NH_4IO_4.3H_2O$; and C. Langlois, crystals of the dihydrated salt, $NH_4IO_4.2H_2O$. The crystalline form of the anhydrous alkali and ammonium metaperiodates, says T. V. Barker, are extraordinarily similar to that of the minerals of the scheelite group, due, no doubt, to the similarity in the type of composition, KIO_4 and $CaWO_4$, just as is also the case with certain other pairs of compounds—*e.g.* calcium carbonate and sodium nitrate; and potassium perchlorate and barium sulphate.

C. F. Rammelsberg found that if a soln. of lithium carbonate be nearly neutralized with periodic acid, a crystalline mass is obtained when evaporated in a warm place.[5] The crystals have the composition **trihydrated lithium dimesoperiodate,** $Li_4I_2O_9.3H_2O$, which can also be regarded as secondary sodium paraperiodate, $Li_2H_3IO_6$. They lose no water at 100°, but 9·28 per cent. is lost at 200°, and at 275° oxygen comes off as well.

Sodium dimesoperiodate, $Na_4I_2O_9.3H_2O$, or *secondary lithium paraperiodate,* $Na_2H_3IO_6$, has been crystallized from a soln. of sodium metaperiodate made alkaline with the hydroxide. F. Ammermüller and G. Magnus[6] prepared it by leading chlorine into a soln. of equal parts of sodium hydroxide and iodate, and crystallizing from the boiling soln.; C. G. Lautsch led chlorine into a soln. of iodine in potashlye, until the dark-red soln. was decolorized; on evaporating, crystals of the salt separated from the soln.; F. Roques and A. Gerngross used a soln. of alkali hypochlorite in place of chlorine. M. Höhnel heated an intimate mixture of an excess of sodium peroxide with iodine (or sodium iodide) in a porcelain crucible until it had become red hot in one part—the flame is removed and the mass becomes hot without the evolution of iodine vapours. The iodide and iodate simultaneously formed are leached out by washing with water. Sodium dimesoperiodate is very sparingly soluble in cold water, and but slightly soluble in hot water. According to A. Rosenheim and E. Löwenthal, this salt is readily soluble in water, 100 grms. of the sat. soln. at 0°, 25°; 40°, and 100° contain respectively 0·104, 0·157, 0·187, and 0·434 mols. of the salt. The sat. soln. have a faint opalescence, but there is no other indication that a colloidal soln. is formed, such as A. Rosenheim and G. Jander found to be the case with sodium tellurate, $Na_2H_4TeO_6$. Sodium dimesoperiodate dissolves readily in nitric acid, and is decomposed by acetic acid,

forming sodium iodate and formic acid. This salt does not lose its water over conc. sulphuric acid—according to C. F. Rammelsberg, it loses 1·92 per cent. of its water at 185°; about 10 per cent. at 220°; and oxygen begins to come off at 270°, and sodium iodate is formed. The residue remaining after it has been sintered is a mixture of sodium iodide and oxide. According to A. Ihre, crystals of **tetrahydrated sodium dimesoperiodate,** $Na_4I_2O_9.4H_2O$, separate when ammonia is added to a soln. of the metaperiodate; they do not absorb carbon dioxide from the atm. A. Ihre obtained monoclinic crystals of what is thought to be **heptahydrated lithium ammonium dimesoperiodate,** $(NH_4)_2Li_2I_2O_9.7H_2O$, by the addition of ammonia to a mixture of lithium nitrate and sodium metaperiodate. Part of the ammonia and water is lost at 100°.

F. Ammermüller and G. Magnus crystallized **potassium dimesoperiodate,** $K_4I_2O_9.9H_2O$, from a soln. of potassium metaperiodate made alkaline with potassium hydroxide: A. Ihre triturated potassium metaperiodate with an alcoholic soln. of potassium hydroxide as long as the metaperiodate dissolved readily. Needle-like crystals which separate from the soln. belong to the triclinic system and have axial ratios, $a:b:c=0·6763:1:0·7125$; $\alpha=97°\ 47·51'$; $\beta=57°\ 35'$; $\gamma=90°\ 12'$. This salt may be the trihydrated *secondary potassium paraperiodate*, $K_2H_3IO_6.3H_2O$. The crystals lose nearly all their water over conc. sulphuric acid. C. F. Rammelsberg and A. Ihre say the crystals are always hydrated. F. Ammermüller and G. Magnus say anhydrous. The dry salt loses from 76 to 77 per cent. of oxygen when melted, and some iodine, forming what C. F. Rammelsberg thought might be an oxyiodide, $2KI.K_2O$; 100 grms. of cold water dissolve 10·3 parts of potassium dimesoperiodate. According to J. Philipp, iodine converts the salt into the iodate and iodide: $K_4I_2O_9+I_2=3KIO_3+KI$; and chlorine converts it into the metaperiodate: $3K_4I_2O_9+3Cl_2=6KClO_4+KClO_3+5KCl$. C. W. Kimmins prepared **tertiary dimesoperiodate,** $3K_2O.2I_2O_7.H_2O$, that is, $K_3HI_2O_9$, by acidifying with a little nitric acid the wash-water and mother liquid obtained in the preparation of potassium metaiodate. The white crystals are very sparingly soluble in water. C. F. Rammelsberg[7] found crystals of trihydrated **ammonium dimesoperiodate,** $(NH_4)_4I_2O_9.3H_2O$, to separate from a soln. of periodic acid in a large excess of ammonia. The colourless crystals belong to the trigonal system with the axial ratio $a:c=1:1·6118$, and $\alpha=78°\ 38'$. These crystals have also been regarded as secondary ammonium paraperiodate, $(NH_4)_2H_3IO$.

A. Ihre[8] prepared sodium **mesoperiodate,** $Na_3IO_4.\frac{3}{4}H_2O$, by mixing a conc. alcoholic solution of sodium hydroxide with a warm conc. soln. of the metaperiodate. E. Müller also made it by the electrolytic oxidation of sodium iodate. Small hexagonal plates separate which absorb moisture and carbon dioxide from the atmosphere. According to C. W. Kimmins, the composition of the sodium salt is $Na_3IO_5.H_2O$. The corresponding **tetrahydrated potassium mesoperiodate,** $K_3IO_5.4H_2O$, *is obtained in a similar manner in rhombohedral crystals which lose* their water at 180°.

C. F. Rammelsberg[9] prepared **lithium paraperiodate,** Li_5IO_6, by the feeble calcination of lithium dimesoperiodate up to the temp. at which the development of iodine commences. When the sintered mass is leached with a little water, some lithium iodide is removed. The salt readily dissolves in water, and furnishes a precipitate of the silver salt when treated with silver nitrate. Trihydrated lithium dimesoperiodate, $Li_4I_2O_9.3H_2O$, may also be regarded as secondary lithium paraperiodate, $Li_2O_3IO_6$. According to A. Rosenheim and E. Löwenthal, if a solution of a mol. of periodic acid be gradually added to one containing two mols. of lithium hydroxide, the precipitate first formed redissolves, and when the soln. is heated on a water-bath, microscopic spherulites of tertiary lithium paraperiodate, $Li_3H_2IO_6$, separate out. The crystals are very sparingly soluble in water, and the soln. has a feeble alkaline reaction towards litmus. If a feebly acid soln. be evaporated over sulphuric acid, bipyramidal crystals of secondary lithium paraperiodate, $Li_2H_3IO_6$, separate. This salt is sparingly soluble in water, and the soln. has a feebly acid reaction towards

litmus. A. Rosenheim and E. Löwenthal altogether failed to prepare C. F. Rammelsberg's $LiIO_4$: and examined the system, $LiOH-H_5IO_6-H_2O$, at 17°, and found that like *das halbkolloide Lithiumtellurate* of A. Rosenheim and G. Jander, the lithium periodates form adsorption compounds whose composition is a function of the concentration of the sodium hydroxide. It is remarkable, however, that with the ratio $Li_2O : I_2O_7 = 5 : 1$, there is virtually no adsorption, and the progress of the curve indicates that the salts Li_4IO_6 may possibly exist, but there are no breaks in the curve corresponding with the formation of such salts. It is very doubtful if the salt Li_5IO_6, which C. F. Rammelsberg claimed to have made, has really been prepared. Dihydrated sodium metaperiodate, $NaIO_4.2H_2O$, can be regarded as **primary sodium paraperiodate,** NaH_4IO_6. The so-called **secondary sodium paraperiodate,** $Na_2H_3IO_6$, can also be regarded as **trihydrated sodium dimesoperiodate,** $Na_4I_2O_9.3H_2O$. P. Walden also prepared what he regarded as normal **sodium paraperiodate,** Na_5IO_6. If the secondary sodium paraperiodate (*i.e.* sodium dimesoperiodate) be crystallized from a strongly alkaline soln., six-sided crystals of tertiary **sodium paraperiodates,** $Na_3H_2IO_6$, are formed; if the soln. is but feebly alkaline, unchanged quadratic plates of the secondary salt separate. This salt was prepared by A. Ihre and C. W. Kimmins. E. Löwenthal and A. Rosenheim examined the system $NaOH-H_5IO_6-H_2O$ at 17°, and found that neither the secondary nor the tertiary sodium paraperiodates showed colloidal characteristics, and that in aq. soln. no salt of higher basicity than the tertiary salt is formed. P. Walden has measured the electrical conductivities of the sodium paraperiodate salts. C. F. Rammelsberg's **secondary ammonium paraperiodate,** $(NH_4)_2H_3IO_6$, may really be the trihydrated ammonium dimesoperiodate, $(NH_4)_4I_2O_9.3H_2O$; similarly the **trihydrated secondary potassium paraperiodate,** $K_2H_3IO_6.3H_2O$, may really be the secondary potassium dimesoperiodate. A soln. of periodic acid when mixed with two eq. of ammonia in 25 per cent. soln., furnishes rhombohedral crystals of rhombohedral secondary ammonium paraperiodate, $(NH_4)_2H_3IO_6$. As C. F. Rammelsberg showed, if the soln. be acidic instead of ammoniacal, it furnishes the metaperiodate, NH_4IO_4. An aq. soln. of the former is alkaline, and one of the latter is acidic towards litmus. A. Rosenheim and E. Löwenthal obtained a still more basic ammonium paraperiodate, $(NH_4)_3H_7(IO_6)_2.2\frac{1}{2}H_2O$, by heating periodic acid with a great excess of 25 per cent. aq. ammonia in a sealed tube to 140°. Crystals are deposited as the soln. cools. Several periodates of organic bases have been prepared.

Silver periodates.—By evaporating a soln. of silver dimesoperiodate in warm nitric acid, F. Ammermüller and G. Magnus [10] obtained orange-yellow crystals of anhydrous **silver metaperiodate,** $AgIO_4$: and C. W. Kimmins obtained the same crystals by heating hydrated silver dimesoperiodate for six hours at 130°. Both C. W. Kimmins and F. W. Ferlunds regard the salt produced by the first-named process as monohydrated silver metaperiodate, $AgIO_4.H_2O$, which loses its water when heated six hours at 130°. When heated the crystals decompose into silver iodide and oxygen. When treated with cold water, they form a straw-yellow powder of trihydrated silver dimesoperiodate, $Ag_4I_2O_9.3H_2O$; with warm water, a red powder of monohydrated silver dimesoperiodate, $Ag_4I_2O_9.H_2O$; and when boiled with water, or nitric acid, a little silver iodate, $AgIO_3$, is formed as a sparingly soluble white powder.

If silver nitrate be treated with a soln. of sodium dimesoperiodate in dil. nitric acid, and the pale greenish-yellow precipitate be washed with water acidified with nitric acid, and then dissolved in warm dil. nitric acid, the soln. furnishes, on cooling, straw-yellow trigonal crystals of **trihydrated silver dimesoperiodate,** $Ag_4I_2O_9.3H_2O$. The same salt is formed when the orange-red crystals of silver metaperiodate are digested with water; and a soln. of potassium dimesoperiodate, acidified with nitric acid.

According to C. W. Kimmins, different salts are obtained by varying the concentration of the nitric acid. If the amount of nitric acid be just sufficient to effect the soln. of the

sodium periodate which is treated with silver nitrate, a dark-brown precipitate of *secondary silver mesoperiodate*, Ag_2HIO_5, will be formed: C. F. Rammelsberg stated that this salt is silver mesoperiodate, Ag_3IO_5, and is also obtained by treating trihydrated silver dimesoperiodate with silver nitrate in the cold, but C. W. Kimmins could only get Ag_2HIO_5. If a slight excess of nitric acid be used to dissolve the sodium salt, a dark-red precipitate of secondary silver paraperiodate, $Ag_2H_3IO_6$, is formed—possibly $Ag_4I_2O_9.3H_2O$—and if a still greater excess of nitric acid be used a slate-coloured precipitate of *tertiary silver paraperiodate*, $Ag_3H_2IO_6$, is possibly formed—but the evidence is not satisfactory. With conc. nitric acid, *monohydrated silver metaperiodate*, $AgIO_4.H_2O$, is formed. Similar results were obtained by C. W. Kimmins by the use of acidified soln. of potassium dimesoperiodate and silver nitrate.

The trigonal crystals of trihydrated silver dimesoperiodate have the axial ratio $a:c=1:2\cdot065$. They become grey on exposure to light; and when heated to 100° for 12 hrs., or repeatedly treated with warm water, they furnish a dark reddish-brown crystalline powder of **monohydrated silver dimesoperiodate**, $Ag_4I_2O_9.H_2O$. The crystals, when heated to 125° (F. W. Ferlunds), 130° (C. W. Kimmins), or 150° (C. F. Rammelsberg), lose their water of crystallization and form a chocolate-brown powder of anhydrous **silver dimesoperiodate**, $Ag_4I_2O_9$. The hydrated forms readily dissolve in warm nitric acid. The silver dimesoperiodates decompose slowly when boiled with water. According to C. G. Lautsch,[11] ammonia precipitates a substance with the composition $Ag_8I_2O_{11}$, which A. Rosenheim and O. Liebknecht and C. G. Lautsch regard as a mixture, not a compound. According to F. W. Ferlunds, if a neutral soln. of a periodate be treated with silver nitrate, or if silver dimesoperiodate be boiled with water for a long time, **silver mesoperiodate**, Ag_3IO_5, is formed. C. F. Rammelsberg considers that F. W. Ferlunds' salt is a mixture of dimesoperiodate and paraperiodate. A. Rosenheim and O. Liebknecht prepared this salt by adding just enough nitric acid to a suspension of sodium paraperiodate in water to dissolve all the salt, and then treating the soln. at 100° with a neutral soln. of silver nitrate; and they also made this salt by treating a boiling soln. of secondary silver paraperiodate in dil. nitric acid with freshly precipitated silver oxide, and filtering through asbestos. Black crystals of **silver mesoperiodate**, Ag_3IO_5, separate out on cooling the soln. According to A. Rosenheim and O. Liebknecht, if secondary silver paraperiodate, $Ag_2H_3IO_6$, be boiled with water; or, according to C. W. Kimmins, if silver nitrate be added to a soln. of sodium paraperiodate containing just sufficient nitric acid to dissolve the sodium salt, the chocolate-brown precipitate is **secondary silver mesoperiodate**, Ag_2HIO_5.

According to C. G. Lautsch, a salt of the composition $(Ag_2O)_4.I_2O_7$ is formed when sufficient trihydrated silver dimesoperiodate is poured into a soln. of nitrate to leave an excess of silver in soln. after the dark brown salt is precipitated. The product may be a mixture: it can be heated to 150° without decomposition, and when the temp. is raised, it melts to a brown mass, and finally forms a mixture of silver and silver iodide. It is insoluble in ammonia; nitric acid gradually converts it into trihydrated silver dimesoperiodate.

C. F. Rammelsberg says that normal **silver paraperiodate**, Ag_5IO_6, is formed by adding silver nitrate to a neutral soln. of an alkali periodate, but A. Ihre, and C. W. Kimmins failed to get this salt by using sodium or potassium dimesoperiodates. C. W. Kimmins obtained what he regarded as **secondary silver mesoperiodate**, Ag_2HIO_5. It is also obtained by boiling the dimesoperiodate with water; or treating it in the cold with silver oxide. A. Rosenheim and O. Liebknecht prepared **normal silver paraperiodate**, Ag_5IO_6, by treating secondary silver paraperiodate, $Ag_2H_3IO_6$, with boiling water. The colour of the precipitate changes from yellow to reddish-brown, and finally black, and the liquid becomes acid. The normal silver paraperiodate then appears as a black crystalline powder; the same compound is formed by treating secondary silver paraperiodate with ammonia. Silver paraperiodate is very dark brown in colour; it is anhydrous and decomposes at about 200°, forming oxygen, silver, and silver iodide. It is soluble in nitric acid

and ammonia. When the nitric acid soln. is conc. by evaporation, crystals of trihydrated silver dimesoperiodate are formed. What is sometimes considered to be **secondary silver paraperiodate,** $Ag_2H_3IO_6$, was first described by F. Ammermüller and *G. Magnus in 1833. It is obtained as a yellowish-green precipitate* by adding silver nitrate to a conc. nitric acid soln. of the sodium salt. A. Rosenheim and O. Liebknecht made it by suspending the sodium salt, $Na_2H_3IO_6$, in water, adding just enough nitric acid to dissolve it, and treating the soln. with neutral silver *nitrate at 20°. It can be recrystallized from dil. nitric acid soln.* This salt may really be the normal **trihydrated silver dimesoperiodate,** $Ag_4I_2O_9.3H_2O$. C. W. Kimmins also claimed to have made the **tertiary silver paraperiodate,** $Ag_3H_2IO_6$, by adding silver nitrate to a soln. of sodium paraperiodate, in a great *excess of nitric acid as previously indicated.*

Copper periodates.—A green powder is obtained when copper carbonate or hydroxide is treated with periodic acid. C. F. Rammelsberg [12] gives the composition $5CuO.I_2O_7.5H_2O$, that is, **pentahydrated cupric paraperiodate,** $Cu_5(IO_6)_2.5H_2O$. *The mother liquor also furnishes a crop of crystals of the same* salt when conc. by spontaneous evaporation, later a crop of dark-green crystals of **hexahydrated cupric dimesoperiodate,** $Cu_2I_2O_9.6H_2O$. This salt loses about 5·18 per cent. of water at 200° and becomes brown. By evaporating mixed soln. of cupric sulphate or nitrate with sodium metaperiodate, M. Bengieser, C. Langlois, and C. G. Lautsch obtained a green mass, which when extracted with water left a bright green crystalline salt which had the composition $4CuO.I_2O_7.H_2O$, that is, **quaternary cupric paraperiodate,** Cu_2HIO_6. C. Langlois also made it by treating copper carbonate with an excess of periodic acid; and C. W. Kimmins, by boiling secondary sodium paraperiodate or potassium dimesoperiodate with cupric sulphate. The green crystals are very soluble in nitric acid, and on evaporating this soln. a bright yellow crystalline salt is formed which has not been identified. **Trihydrated secondary silver paraperiodate,** $CuHIO_6.3H_2O$, is formed from mixed soln. of cupric nitrate and sodium metaperiodate. A. Werner regards this salt as *tetrahydrated hexolcupric periodate*, $[Cu(HO.Cu.OH)_3](IO_4)_2.4H_2O$. F. Giolitti has prepared **copper diparaperiodate,** $Cu_4I_2O_{11}.H_2O$, by adding sodium metaperiodate to copper sulphate or nitrate, or secondary potassium mesoperiodate, K_2HIO_5, to copper acetate. It is a greenish-yellow powder, which becomes anhydrous at 120°. **Copper metaperiodate,** $Cu(IO_4)_2$, is formed as a sky-blue precipitate by boiling a mixture of copper acetate and periodic acid, and the three **copper paraperiodate** salts, $Cu_5(IO_6)_2.7H_2O$, $Cu_5(IO_6)_2.5H_2O$, and $Cu_5(IO_6)_2.3H_2O$, are known. The first is obtained as a green powder by adding an excess of copper acetate to secondary potassium mesoperiodate, K_2HIO_5, and boiling the precipitate with ammonia; the second as a green powder by dissolving copper carbonate in aq. periodic acid; and the third as a yellowish-green powder by dissolving copper dimesoperiodate in nitric acid, and boiling the liquid with cupric hydroxide.

The periodates of the alkaline earths.—C. F. Rammelsberg [13] obtained **calcium metaperiodate,** $Ca(IO_4)_2$, by the action of periodic acid on a soln. of calcium hydroxide or dimesoperiodate, the solid separates on concentrating the acid soln.; similarly, when a soln. of strontium carbonate in an excess of periodic acid is conc. in a desiccator, large, probably triclinic, crystals of **hexahydrated strontium metaperiodate,** $Sr(IO_4)_2.6H_2O$, are formed. They lose 12·36 per cent. of water when conc. over conc. sulphuric acid, and the remainder at 100°. This salt explodes when heated; the aq. soln. has an acid reaction, and gives a precipitate when treated with ammonia. When the attempt is made to concentrate the soln. of **barium metaperiodate,** $Ba(IO_4)_2$, prepared in a similar manner, the dimesoperiodate is deposited when the soln. is conc., so that the metaperiodate has not been isolated in a solid state.

If an alkali periodate be treated with a soln. of a barium salt, C. F. Rammelsberg [14] *says that the soln. becomes more and more acid with sodium periodate:* $2NaIO_4+2Ba(NO_3)_2+H_2O=Ba_2I_2O_9+2NaNO_3+2HNO_3$; but with potassium dimesoperiodate the soln. remains neutral. The voluminous precipitate soon

becomes crystalline, and is said to be barium dimesoperiodate, $Ba_2I_2O_9.7H_2O$, although the evidence is not decisive whether there are 6, 7, or 8 molecules of water of hydration. The same salt is precipitated when baryta water is dropped into periodic acid until the mixture is distinctly acid; and, according to C. Langlois, when baryta water is added to a soln. of sodium dimesoperiodate. The hydrate loses water at 100°, leaving a residue which approximates to $Ba_2I_2O_9.3H_2O$; and at 240° it forms the anhydrous salt which decomposes at a higher temp., giving off oxygen and forming barium iodate, $Ba(IO_3)_2$; and at a still higher temp. barium paraperiodate, $Ba_5(IO_6)_2$. According to H. A. Auden and G. J. Fowler, when heated to 388° in an atm. of nitric oxide, NO, the salt is decomposed, giving off much iodine and forming barium iodide. The hydrated salt is soluble in nitric acid, and, according to H. Kämmerer, is not decomposed by a mixture of ammonia and ammonium carbonate, nor by boiling with ammonium sulphate or oxalate. The corresponding **strontium dimesoperiodate,** $Sr_2I_2O_9$, was made by C. Langlois, and C. F. Rammelsberg in a similar manner; and **calcium dimesoperiodate,** $Ca_2I_2O_9$, with 7 or 9 molecules of water of hydration was obtained by M. Bengieser and C. Langlois. The white prismatic crystals of the hydrate become anhydrous at 200° to 250°. The crystals are soluble in water.

When a soln. of calcium dimesoperiodate is treated with ammonia, a gelatinous precipitate is formed to which C. F. Rammelsberg attributed the formula $8CaO.3I_2O_7+Aq$; A. Ihre obtained a mixture of two compounds under these conditions. With barium dimesoperiodate, C. F. Rammelsberg stated that reddish crystals, corresponding with $5BaO.3I_2O_7.18H_2O$, are formed. C. F. Rammelsberg (1868) and C. G. Lautsch also reported a compound $5BaO.2I_2O_7.5H_2O$. These precipitates are probably mixtures of oxide and periodate.

A. Ihre prepared **barium mesoperiodate,** $Ba_3(IO_5)_2$, and also **strontium mesoperiodate,** $Sr_3(IO_5)_2$, by adding ammonia to a dil. aq. soln. of sodium metaperiodate, and dropping the mixture into a soln. of barium or strontium nitrate as the case might be: $3Sr(NO_3)_2+2Na_4I_2O_9=Sr_3(IO_5)_2+2NaIO_4+6NaNO_3$.

When barium iodate is heated to a high temp., C. F. Rammelsberg[15] found that a basic periodate, $5BaO.I_2O_7$, that is, normal **barium paraperiodate,** $Ba_5(IO_6)_2$, is formed: $5Ba(IO_3)_2=Ba_5(IO_6)_2+4I_2+9O_2$. Normal **strontium paraperiodate,** $Sr_5(IO_6)_2$, and normal **calcium paraperiodate,** $Ca_5(IO_6)_2$, are formed in a similar way. When the yellow mass is leached with water it yields up to one per cent. of barium iodide, and the white residue is insoluble in water and soluble in dil. nitric acid. The soln. in nitric acid gives a precipitate of normal silver paraperiodate, Ag_5IO_6, with silver nitrate. The yellow mass obtained by calcining the iodate has been stated to contain a compound of barium iodide with barium peroxide, which forms the periodate when treated with water. For if an intimate mixture of barium iodide and barium peroxide be heated in a long-necked flask, the mixture melts and reacts vigorously, much iodine is evolved, and a yellow mass is finally obtained, which, according to C. F. Rammelsberg, has the composition $I.2BaO_2$, and which, when treated with water, forms the periodate: $16Ba_2IO_4+4H_2O=4Ba(OH)_2+3BaI_2+5Ba_5(IO_6)_2$. C. F. Cross and S. Sigiura found that when the vapour of iodine in a stream of dry air, is passed over the oxides or carbonates of the alkaline earths, periodates are formed, but no iodide or oxyiodide. Similarly, by heating barium iodide in a stream of dry air until no more iodine is given off, 0·173 grm. of the iodide yielded 0·098 grm. of the periodate: $5BaI_2+6O_2=4I_2+Ba_5(IO_6)_2$. Hence, under the conditions of these experiments, barium paraperiodate is the most stable compound of the three elements concerned. Barium carbonate and iodine vapour do not yield the periodate if air be excluded; and the formation of periodate begins only when dry air is admitted. Hence, say C. F. Cross and S. Sigiura, the formation of periodate is here referable *not* to the direct replacement of oxygen by iodine, and the subsequent oxidation of the iodide thus formed, but rather to the oxidation of iodine itself (a supply of nascent oxygen being determined by the presence of air and barium oxide), and the union of the oxidized

iodine with barium oxide. Similar remarks apply to the action of iodine vapour and dry air on strontium and calcium oxides, but in a less marked degree, owing to the inferior stability of the products. Barium paraperiodate is decomposed when heated in a stream of hydrogen, forming water and a mixture of barium iodide and oxide.

The periodates of beryllium, magnesium, zinc, cadmium, and mercury.—A. Atterberg[16] reported the formation of crystalline plates of **beryllium mesoperiodate,** $Be_3(IO_5)_2$, with 11 and 13 molecules of water of hydration, the former, by crystallization from the soln. of beryllium carbonate in periodic acid; and the latter, by adding beryllium sulphate to the mother liquor which remains. The crystals are not very soluble in water; they dissolve in nitric acid; both hydrates lose water at 100°, leaving $5H_2O$ still combined; and on boiling with water they decompose, forming a basic salt which remains undissolved, and an acid salt which passes into soln., and which gives a glassy mass when evaporated to dryness. A soln. of magnesium carbonate in periodic acid furnishes a sparingly soluble hydrated residue, $4MgO.I_2O_7$, and a soln. which furnishes crystals of **magnesium metaperiodate,** $Mg(IO_4).10H_2O$, which are soluble in water, and have an acid reaction.[17] C. Langlois obtained **magnesium dimesoperiodate,** $Mg_2I_2O_9$, with 12 (C. Langlois) or 15 (C. F. Rammelsberg) molecules of water of crystallization, in small prismatic crystals—probably monoclinic—by concentrating a neutral soln. of magnesium carbonate in periodic acid. C. F. Rammelsberg obtained the same compound from the soln. obtained by mixing sodium mesoperiodate and magnesium sulphate. The crystals lose water about 100°, leaving a residue approximating $Mg_2I_2O_9.3H_2O$; the water of hydration is not lost over conc. sulphuric acid. If a feebly acid soln. of magnesium carbonate in periodic acid be evaporated, in addition to magnesium dimesoperiodate, and metaperiodate, crystals of **magnesium diparaperiodate,** $Mg_4I_2O_{11}.6H_2O$, are formed; or maybe the acid mother liquid, remaining after the separation of the dimesoperiodate, gives an amorphous precipitate of approximately $Mg_4I_2O_{11}.9H_2O$, when partially neutralized with sodium carbonate.

The periodates of zinc reported by C. Langlois and C. F. Rammelsberg[18] are not well defined; many appear to be basic precipitates, and there are reasons for doubting their individuality, since their composition is based upon chemical analysis alone. By treating zinc oxide with a slight excess of periodic acid, C. F. Rammelsberg obtained white pulverulent **hexahydrated zinc dimesoperiodate,** $Zn_2I_2O_9.6H_2O$; and C. Langlois by using zinc carbonate in periodic acid prepared **zinc diparaperiodate,** $Zn_4I_2O_{11}.H_2O$, and a soln. of this salt in periodic acid gave crystals of the basic salt, $3ZnO.2I_2O_7.7H_2O$, which A. Ihre believes is not a mere mixture. C. F. Rammelsberg prepared the basic salt: $5ZnO.2I_2O_7.14H_2O$, by the double decomposition of zinc sulphate and sodium periodate; and, by adding ammonia to the mother liquor, obtained an amorphous precipitate: $9ZnO.2I_2O_7.12H_2O$.

C. F. Rammelsberg[19] reported the formation of **cadmium metaperiodate,** $Cd(IO_4)_2$, as an anhydrous white powder, when cadmium carbonate is treated with hot periodic acid, and the precipitate washed and dried; if a little free acid be present, **trihydrated cadmium diparaperiodate,** $Cd_4I_2O_{11}.3H_2O$, is said to be formed. The white precipitate formed when sodium metaperiodate is dropped into cadmium sulphate is said to furnish **pentahydrated cadmium mesoperiodate,** $Cd_3(IO_5)_2.5H_2O$, when washed in cold water and dried in air; and the mother liquor when evaporated spontaneously gives small rhombic crystals of **enneahydrated cadmium dimesoperiodate,** $Cd_2I_2O_9.9H_2O$, with the axial ratios $a:b:c=0.595:1:0.795$. The crystals are not soluble in water, and form the yellow dipara-salt when boiled in water. C. W. Kimmins treated secondary sodium diparaperiodate or potassium dimesoperiodate with cadmium sulphate, and he considered the resulting brown powder to be **secondary cadmium mesoperiodate,** $CdHIO_5$; the analysis agrees equally well with $Cd_2I_2O_9.H_2O$.

M. Bengieser[20] and C. F. Rammelsberg obtained a yellow precipitate of mercurous periodate by treating a soln. of mercurous nitrate with sodium metaperiodate

C. G. Lautsch uses a soln. of sodium dimesoperiodate acidified with a drop of nitric acid in place of sodium metaperiodate. According to C. G. Lautsch, the precipitate is **mercurous paraperiodate** Hg_5IO_6, and, according to C. F. Rammelsberg, *mercurous diparaperiodate*, $Hg_9I_2O_{11}$. It is soluble in nitric acid, and the mercurous salt becomes mercuric; ammonia converts the precipitate into a black powder. Sodium metaperiodate gives a precipitate of **mercuric diparaperiodate,** $Hg_4I_2O_{11}$, when treated with mercuric nitrate, but not with mercuric chloride. C. G. Lautsch used sodium dimesoperiodate in place of the metaperiodate; the same salt is made by treating freshly precipitated mercuric oxide with periodic acid. This salt is reddish-orange, soluble in hydrochloric acid; less soluble in nitric acid. When the soln. in nitric acid is much dil. with water, the salt is reprecipitated in the crystalline state. An excess of ammonia redissolves the precipitate. If a soln. of potassium dimesoperiodate be gradually added to an aq. soln. of mercuric chloride, a bright orange-red precipitate is formed.[21] The precipitate retains its colour when dried at 100°; and it has an empirical composition corresponding with $5K_2O.10HgO.6I_2O_7$.

A. S. Eakle[22] crystallized **trihydrated aluminium metaperiodate,** $Al(IO_4)_3.3H_2O$, from nitric acid soln. in colourless octahedra. P. T. Cleve[23] precipitated a white microcrystalline **dihydrated lanthanum mesoperiodate,** $LaIO_5.2H_2O$, by adding periodic acid to a soln. of lanthanium acetate, but not lanthanum nitrate. P. T. Cleve also obtained an amorphous precipitate of **tetrahydrated samarium mesoperiodate,** $SmIO_5.4H_2O$, of sp. gr. 3·793 at 21·2°. With yttrium acetate, two **yttrium periodates** were obtained; the first is formed as an amorphous and white precipitate: $3Y_2O_3.2I_2O_7.6H_2O$, by adding an excess of yttrium nitrite to periodic acid; yttrium acetate gives a precipitate with periodic acid, which dissolves in an excess of the acid, and the soln. furnishes microcrystals of **tetrahydrated yttrium mesoperiodate,** $YIO_5.4H_2O$.

C. F. Rammelsberg[24] obtained a pale-brown insoluble **thallic periodate,** $3Tl_2O_3.I_2O_7.30H_2O$, by the action of periodic acid on thallic oxide, Tl_2O_3. The compound is decomposed by potash lye; *thallous periodate* has not been made. A yellowish-white precipitate is formed when thallous hydroxide is treated with periodic acid, or when sodium dimesoperiodate is added to the soln. of a thallous salt. The precipitate is reddish-yellow when dried, and appears to be a mixture of thallous and thallic iodates.

The periodates of lead reported by C. F. Rammelsberg are prepared by methods which are so empirical[25] that the individuality of the products cannot in many cases be regarded as established. The salt, $3PbO.I_2O_7.2H_2O$—may be **dihydrated lead mesoperiodate,** $Pb_3(IO_5)_2.2H_2O$; or *lead diparaperiodate*, $Pb_3H_4(IO_6)_2$—is obtained as a white crystalline powder when lead nitrate is treated with potassium dimesoperiodate, or sodium paraperiodate. It becomes yellow when heated, and at 140° very little water is lost; and on further heating it decomposes into iodine, oxygen, water, lead iodide, and oxide. F. Giolitti prepared **monohydrated lead mesoperiodate,** $Pb_3(IO_5)_2.H_2O$, by boiling a soln. of secondary lead mesoperiodate in dil. nitric acid with lead oxide. According to C. W. Kimmins, it forms the anhydrous salt, $Pb_3(IO_5)_2$, after being heated for some hours at 275°. Dihydrated lead mesoperiodate is sparingly soluble in water, readily soluble in nitric acid; and if the nitric acid soln. be concentrated, it furnishes a dark yellow powder of lead mesoperiodate, $Pb_3(IO_5)_2$; the same salt is obtained when lead nitrate is added to nitric acid soln. of the alkali periodates. Anhydrons lead mesoperiodate is very hygroscopic, the dihydrated salt is not. C. W. Kimmins obtained **lead metaperiodate,** $Pb(IO_4)_2$, by boiling lead mesoperiodate with nitric acid for some time, a small quantity of an amorphous red salt being obtained which is difficult to separate completely from the yellow mesoperiodate. F. Giolitti regards the precipitate which is formed when a soln. of lead acetate, acidified with acetic acid, is added to a cold soln. of potassium mesoperiodate, not as the mesoperiodate, $Pb_3(IO_5)_2.2H_2O$, but as secondary lead mesoperiodate, $PbHIO_5.H_2O$. F. Giolitti

also prepared **quaternary lead paraperiodate,** Pb_2HIO_6, by boiling the mesoperiodate with water for a long time.

P. T. Cleve[26] prepared an insoluble **thorium periodate** by adding periodic acid to a thorium salt soln.; and periodic acid produces a precipitate of **cerous periodate** when added to cerous acetate. The precipitate rapidly becomes yellow.

C. F. Rammelsberg[27] (1868) failed to make manganese periodate; he found that when an alkali periodate is added to a soln. of a manganese salt, or periodic acid to manganese carbonate, a mixture of hydrated manganese dioxide and manganous iodate is formed. W. B. Price obtained an intense red precipitate when a soln. of alkali periodate or periodic acid strongly acidified with sulphuric (or nitric) acid is added to a soln. of manganese sulphate (or nitrate) strongly acidified with sulphuric (or nitric) acid. The precipitate forms slowly in the cold, rapidly at 45°. In this way W. B. Price prepared **manganato-sodium diparaperiodate,** $Na_2Mn_2I_2O_{11}$; equivalent to $Na_2I_2O_{11}.Mn_8(I_2O_{11})_3$, or to $Na_2O.Mn_2O_3.I_2O_7$, manganese tervalent; **manganato-potassium diparaperiodate,** $K_2Mn_2O_2I_{11}$. The precipitate does not develop in neutral soln., it is not acted on by boiling water or boiling acid; and an excess of manganese salt acts as a reducing agent. These salts may be regarded as diparaperiodates, derivatives of diparaperiodic acid, $H_8I_2O_{11}$, with six hydrogen atoms displaced by two tervalent manganese atoms. They may also be regarded as complex salts of a **manganato-periodic acid,** $H_2Mn_2I_2O_{11}$, evidence of the formation of which is obtained with soln. containing a great excess of free acid. This acid may be regarded as **manganic diparaperiodate.** C. F. Rammelsberg[28] found that when uranium tetrachloride is treated with potassium periodate, a greenish-grey precipitate of **uranous periodate** is formed, which soon passes into yellowish-white **uranyl periodate.** According to C. F. Rammelsberg,[29] the pale yellow precipitate obtained by M. Bengieser by adding potassium periodate to a ferrous salt is not *ferrous periodate*, as was at first supposed, but rather a ferric periodate. This salt is soluble in nitric acid. **Ferric mesoperiodate,** $FeIO_5.11H_2O$, appears as a yellowish-brown precipitate when a ferric salt is treated with potassium periodate. C. W. Kimmins, however, claims to have prepared **ferrous paraperiodate,** $Fe_5(IO_6)_2$, as a brick-red precipitate, by adding a soln. of potassium dimesoperiodate to ferrous sulphate and a light-brown powder of secondary ferrous paraperiodate, FeH_3IO_6, by adding a soln. of secondary sodium paraperiodate to ferrous sulphate. On treating secondary sodium paraperiodate, or potassium dimesoperiodate, with ferric chloride, a light-brown precipitate is formed, which, when dried at 100°, is a reddish-brown powder which has a composition corresponding with **tertiary ferric dimesoperiodate,** $FeHI_2O_9$. Boiling dil. nitric acid has no appreciable effect on the salt, but when boiled with conc. nitric acid, it forms **ferric metaperiodate,** $Fe(IO_4)_3$, as a yellow powder.

C. F. Rammelsberg[30] (1868) found that when nickel carbonate is treated with periodic acid, a green soln. is obtained, and a mixture of nickel dioxide, iodate, and periodate remains undissolved; when the green soln. is evaporated at a very low temp., or over conc. sulphuric acid, pale green quadratic prisms are formed. The analyses are not satisfactory, varying from $7NiO.4I_2O_7+(49 \text{ to } 63)H_2O$. The crystals are insoluble in water, soluble in periodic acid. When the soln. is heated it forms nickel hydroxide and nickel iodate. C. W. Kimmins has reported **nickel mesoperiodate,** $Ni_3(IO_5)_2$, as a greenish-yellow amorphous precipitate formed by treating a nickel sulphate with secondary sodium paraperiodate. No action occurs in the cold, but on boiling a flocculent precipitate separates from the soln. A bluish-green gelatinous precipitate is formed when a soln. of potassium dimesoperiodate is treated with nickel sulphate; when dried at 100°, the black crystalline salt **nickel dimesoperiodate,** $Ni_2I_2O_9$, is formed. No other salt was obtained by boiling the nickel periodates down with nitric acid. C. G. Lautsch[31] obtained a greenish-yellow powder on evaporating a soln. of sodium periodate with an excess of cobalt sulphate to which the composition $7CoO.2I_2O_7$ has been assigned

C. F. Rammelsberg failed to prepare a *cobalt periodate*, but always obtained a mixture of oxide and iodate.

Complex acids and salts.—Periodic acid forms a series of complex salts and acids similar to those obtained with iodic acid. Chromato-compounds have not yet been prepared, but three series of molybdato- and tungstato-periodates are known. A. Rosenheim and O. Liebknecht [32] and C. W. Blomstrand have made alkali **hexamolybdato-periodates** of the type formula, $5M_2O.I_2O_7.12MoO_3$; and the **hexatungstato-periodates** of the alkalies and alkaline earths with the type formula, $5M_2O.I_2O_7.12WO_3$; C. W. Blomstrand has made **ammonium tetramolybdato-periodate,** $4(NH_4)_2O.I_2O_7.8MoO_3.7H_2O$; and A. Rosenheim and O. Liebknecht and C. W. Blomstrand have made sodium and ammonium **monomolybdato-periodates,** $3M_2O.I_2O_7.2MoO_3.8H_2O$; and ammonium and sodium **monotungstato-periodates,** $3M_2O.I_2O_7.2WO_3$. R. F. Weinland and O. Koppen have made **cæsium fluoro-periodate,** $2CsIO_4.3HF.H_2O$, analogous to the fluoroiodates.

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CHAPTER XX

THE ALKALI METALS

§ 1. The History of the Alkali Metals

The burning matter of salt has greater affinity for other substances still more foreign with which it will combine, leaving the metal of salt pure. The transmutation of salt is affected by much craft and cunning, leaving a good metal the result, and which is like no other metal, but the art is not known to common men.—ROGER BACON (c. 1250).

THE cleansing properties of an aq. extract of the ash of vegetable matter were known to the ancients; it was also known that the filtered or decanted liquid is charged with a salt which remains at the bottom of the vessel after the evaporation of the water. This salt was called *neter*. Jeremiah (**2**. 22) referred to this substance in the seventh century before our era. His term *neter*, translated *nitre*, is derived by the scholars from *natar*, which makes *neter* or *nitre* mean a substance which effervesces. In one of Solomon's sharpest *Proverbs* (**25**. 20), the reference to the commotion which ensues on mixing nitre with vinegar shows that *natron*, what we now call sodium carbonate, was in the writer's mind. The *neter* of the Hebrews, the *nitre* of the translators, the *nitron*—*νίτρον*—of the Greeks, and the *nitrum* of the Romans, thus refer to the same thing.

In his *Meteorology*, Aristotle said that the Umbrians extracted a salt from the ashes of reeds and bulrushes. Other references in the writings of Aristotle, Dioscorides, and Pliny[1] leave no doubt that the term *nitrum* referred to impure forms of potassium carbonate. For example, we are told that *nitrum* was obtained by the lixiviation of the ashes of the oak, wine-lees, the vine, and other plants which we know to furnish impure potassium carbonate—*cineres clavellati*—and in some cases, sodium carbonate; the impure sodium carbonate derived from the trona deposits and saline lakes of Egypt was also called *nitrum*. The saline efflorescence on walls—*sal murale*—must have been noticed at a very early period, and the ancients, who sought medicinal virtues in all natural bodies, must have collected and examined the properties of this saline mass which they also called *nitrum*. The alkaline efflorescence of the soils in hot countries was lixiviated from the earth, and called *nitrum*. These efflorescences contained variable amounts of saltpetre. Four different substances—potassium and sodium carbonates or nitrates—were thus confused under one term. The ancients, indeed, were very prone to include many different substances under one name, even when these substances corresponded with one another only in a few accidental particulars; in some cases, also, special terms were employed to designate not different substances but accidental varieties of one substance.

There can be no doubt that the *nitrum* of ancient writings must have been in some cases an alkaline carbonate, which in their nomenclature was confused with saltpetre. It is not known when saltpetre was definitely recognized as something different from the ordinary *nitrum*. It is commonly supposed that saltpetre was a component of Greek fire invented near the end of the seventh century. The first definite reference to saltpetre appears in literature in connection with the preparation of gunpowder. Albertus Magnus and Roger Bacon, of the thirteenth century, both refer to this salt, and probably both derived their information from

the same Arabian sources. It is not improbable that gunpowder was invented by the Hindus, for, in their country, saltpetre occurs abundantly in the village soils. The recipe for gunpowder was probably brought into Europe by the Saracens *viâ* Africa about the twelfth or thirteenth century. About this time too the term *sal petræ*—the salt of the rock—came to be applied particularly to that form of *nitrum* which alone could be used as one of the chief ingredients of gunpowder, and Greek fire. The later alchemists also employed the term *sal nitri* for the same salt. According to J. Beckmann, the term *natron* or *natrium* arose from a modification of the pronunciation of the old term *nitrum* in the *patois* of the East. The term *natron* was then applied to the native *nitrum* (sodium carbonate), and the latter term, altered to *nitre*—a synonym for *saltpetre*—was reserved for *sal petræ*.

The term *natron* first appeared in European writings [2] towards the end of the sixteenth century, although *natrum* was used in the tenth century for the mineral alkali by the Persian writer Abu Mankur Muwaffak in a work on *The principles of pharmacology* (Hirow, 975).[3] The half-vitrified ashes of certain plants, *e.g.* glasswort, were cultivated and introduced by the Arabians into Europe for making glass, soap, dyes, etc. Those plants first used were called by various names, *e.g.* *herba kali*, where *kali* is the Arabian term for ashes—*kalay*, to roast.

The scholars tell us that the term *kali* was probably derived by the Arabians from the Sanscrit. It appears to have been the Hindu name for a destroying goddess who had numerous arms and red-palmed hands; her eyes were red, and her face and breasts were besmeared with blood. The name Calcutta is derived from Kalighat, meaning "Kali's landing-place."

The term *kali* with the *al* prefix referred to the half-vitrified ashes, and hence the salts obtained from the ashes of plants were called *alkaline salts* as well as *nitrum*. The term *sal alchali* for the ashes of sea-plants appears in the writings of the Latin Geber about the thirteenth century; and the same term was also employed for the ashes of land-plants. It is known that the former furnishes a large proportion of sodium carbonate, the latter potassium carbonate. Later on, in order to distinguish these salts from ammonium carbonate, they were termed **fixed alkalies,** and ammonium carbonate was called **volatile alkali.**

The difference in the two forms of fixed alkali—if it was noticed at all—attracted no particular attention until J. Bohn [4] (1683) found that two different kinds of crystals of saltpetre were obtained from salt and from wood ashes; and G. E. Stahl (1702) showed that the alkali in common salt is different from that in wood ashes. H. L. Duhamel du Monceau (1736) also recognized a difference between potash and soda; but A. S. Marggraf (1762) demonstrated clearly the essential difference between the properties of these two bases. He noted that the sulphates obtained by the action of sulphuric acid on common salt and on the fixed alkali obtained from wood ashes, are different—the former is more soluble in water than the latter. The nitrate derived from the base of common salt crystallizes in cubes; the nitrate from vegetable alkali crystallizes in prisms. The former colours a flame yellow, the latter blue. The chloride of mineral alkali is common salt; the chloride of vegetable alkali is the *digestive salt of Sylvius*. The carbonate of the mineral alkali is not deliquescent in air, the carbonate from vegetable alkali is deliquescent. The two alkalies were distinguished by using the term **vegetable alkali** for potassium carbonate, and **mineral alkali** for sodium carbonate. It was generally supposed that the alkali occurred only in burnt plants, but in 1781, J. C. Wiegleb showed that the alkali is present in fresh plants. When M. H. Klaproth (1797) [5] showed that the *Pflanzenalkali*—vegetable alkali—occurred in many minerals, the term *potash* (English) or *potasse* (French), was applied to this particular base; the word is a corruption of *pot-ash*—the ash or residue of the pot—in reference to the preparation of *nitrum* by the evaporation [6] in pots of the clear lixivium from wood ashes. The Germans use the term *Kali*. M. H. Klaproth also proposed to confine

the term *natron* to mineral alkali, sodium carbonate. The English eq. for natron is *soda*, and the French, *soude*. The word *soda* is supposed to be derived from the Latin *solida*, a solid, through the Italian *soda*, a term applied in the Middle Ages to all alkalies, and particularly to the ashes of the glasswort, barilla, or salsola, which were used in making glass and soap. The first letter of the word *kali* is used by all chemists as the symbol for potassium and the first two letters of the word *natron* for sodium.

The chemists or alchemists gradually acquired a knowledge of the various salts produced by the action of acids on *nitrum*; and of the transformations of the various salts from one form to another, by the action of acids on the different salts—*e.g.* sulphuric acid on sodium chloride. The carbonates of the alkalies were called *mild alkalies* to distinguish them from the *caustic alkalies*. It was known quite early that the caustic alkalies are obtained by the action of quicklime on the mild alkalies; for example, the Latin Geber [7] and Albertus Magnus of the thirteenth century knew that the ash of plants furnished a caustic alkali when treated with quicklime and water. The process is essentially that employed to-day.

Potassium and sodium.—A. L. Lavoisier [8] regarded the alkalies and earths as simple substances which, with increasing knowledge, may prove to be complex. In the second part of his *A New System of Chemical Philosophy* (London, 1810), J. Dalton considered the metallic oxides potash and soda to be simple elements, and the metals potassium and sodium to be compounds of potash or soda with hydrogen. H. Davy refuted J. Dalton's argument, and later remarked:

> In my opinion, Mr. Dalton is too much of an *Atomic Philosopher*, and in making atoms arrange themselves according to his own hypothesis, he has often indulged in vain speculation . . . the essential and truly useful part of his doctrine . . . is perfectly independent of any views respecting the ultimate nature either of matter or its elements.

We are told by H. Davy that, in 1790, M. Tondi attempted to obtain the constituent elements of these earths by heating a mixture of the oxide with carbon. In some cases he obtained metallic reguli. H. Davy also pointed out that G. E. Stahl approached very nearly to the discovery of the pure alkalies, for he exposed a mixture of solid caustic potash and iron filings to a long-continued heat, and stated that in this way an intensely caustic alkali—*valde causticum*—is produced. The oxides were not definitely resolved into their elements until 1807, when H. Davy isolated potassium and sodium by the electrolysis of their hydroxides.

About the middle of the thirteenth century, Roger Bacon, in his *Ars Omnia*, made some references to the *metal of salt*,[9] and this has been considered to refer to the early discovery of the metal sodium. Roger Bacon also said that the "metal of salt" can transmute other metals into gold. This, adds G. F. Rodwell, proves that no reliance can be placed on the assertion; and, further, since the same writer, in his *De mirabili potestate artis et naturæ*, seems to hint at the steam or some equivalent engine, at a diving apparatus, at a flying machine, and at a kind of *elixir vitæ*, it might be maintained with equal force that these engines and specifics were likewise known to the ancients. If one statement be accepted literally, other statements made by the same author under like conditions have a right to similar treatment. This leads to palpable absurdities.

> To take an individual passage from an obscurely written work, and to found on it the claims of its author to some great discovery attributed to a much later period, is a very pernicious practice, and can lead to no good result.

Lithium.—Lithium oxide was discovered by A. Arfvedson, in 1817,[10] while analyzing the mineral petalite. His report was entitled: *Untersuchungen einiger bei der Eisen-Grube von Utö vorkommenden Fossilien und von einem darin gefundenen neuen feuerfesten Alkali.* He found the sodium to be contaminated by an alkali which, unlike potassium, was not removed as a precipitate by treatment with tartaric acid, and, unlike sodium, it formed a sparingly soluble carbonate The

name lithium is derived from the Greek λίθιος—stony—because it was believed, at the time of its discovery, that its presence was confined to the mineral kingdom, but R. Bunsen and G. Kirchhoff showed that the element is generally distributed in the animal and vegetable kingdoms, as well as in the mineral kingdom. A. Arfvedson's discovery was confirmed by L. N. Vauquelin in 1818. A. Arfvedson and C. G. Gmelin failed to isolate the metal by heating the oxide with iron or carbon; or by the electrolysis of its salts—probably because too weak an electric current was employed. H. Davy succeeded in isolating a minute quantity of the metal by the electrolysis of lithium chloride; and in 1855, R. Bunsen and A. Matthiessen obtained the metal in quantity, and examined its chief properties.

Cæsium and rubidium.—R. Bunsen and G. Kirchhoff (1860),[11] while investigating the mineral waters of Durkein (Palatinate), evaporated down 40 tons of the water, and removed the alkaline earths, and lithia with ammonium carbonate. The filtrate showed the spectral lines of sodium, potassium, and lithium, "and besides these, two splendid blue lines" near to the blue strontium line. R. Bunsen and G. Kirchhoff add:

> As no elementary body produces two blue lines in this portion of the spectrum, we may consider the existence of this hitherto unknown alkaline element was thus placed beyond doubt. The facility with which a few thousandths of a milligram of this body may be recognized by the bright blue light of its incandescent vapour, even when mixed with large quantities of more common alkalies, has induced us to propose for it the name cæsium (and the symbol Cs), derived from the Latin *cæsius*, used to designate the blue of the clear sky.

Although spelt *cæsium*, the true spelling should be *cœsium*,[12] as originally done by R. Bunsen, in conformity with the orthography of the Latin term. Thus, in his *Noctes Atticæ* (2. 26), Aulus Gellius said: *Nostris autem veteribus cæsia dicta est, quæ a Græcis, γλαυκῶπις, ut Nigidus ait, de colore cœli quasi coelia.*

Again, R. Bunsen and G. Kirchhoff found on extracting the alkalies from lepidolite (Saxony), and washing the precipitate obtained by treating the soln. of the alkalies with hydrochloroplatinic acid with boiling water a number of times, the residue finally gives "two splendid violet lines" between those due to strontium and to potassium, as well as a number of other lines in the red, yellow, and green portions of the spectrum. R. Bunsen and G. Kirchhoff say:

> None of these lines belong to any previously known body. Amongst them are two which are particularly remarkable in lying beyond Fraunhofer's line in the outermost portion of the red solar spectrum. Hence we propose for this new metal the name rubidium (and the symbol Rb), from the Latin *rubidus*, which was used to express the darkest red colour.

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§ 2. The Occurrence of the Alkali Metals

According to the estimate of F. W. Clarke (1916),[1] the rocks, etc., of the half-mile crust of the earth contains the following percentage amounts:

	Igneous rocks.	*Shales.*	*Sandstones.*	*Limestones.*	*Average.*
Soda, Na_2O	3·36	1·30	0·45	0·05	3·25
Potash, K_2O	2·99	3·24	1·31	0·33	2·98
Lithia, Li_2O	0·01	—	—	—	0·01

and from the average composition of the known terrestrial matter that there is present 2·36 per cent. of sodium and 2·28 per cent. of potassium. The data for cæsium and rubidium are not complete enough to enable reliable estimates to be made of the relatively small quantities present in the earth's crust. According to E. Pringsheim, there is no evidence of the existence of rubidium or cæsium in the sun; there are very faint lines of potassium; while lithium and sodium are well represented in the spectral lines. S. Datta has established the presence of potassium in the sun.

Potassium and sodium.—Potassium and sodium occur in the various soda and potash salts indicated in the list of minerals in the Stassfurt deposits. The alkalies also occur in sea water, in the water of the inland lakes, and in the waters of various springs—Tables XIV and XV. There are also tremendous deposits of rock salt—sodium chloride—in various parts of the world; in Chili and Peru, there are the deposits of soda nitre, $NaNO_3$, which also contain some potash salts; in Greenland there are the deposits of cryolite, $3NaF.AlF_3$; and in the sites of many dried-up lakes there are deposits of sodium carbonate, sodium sulphate, or sodium calcium borates. In India, Egypt, Persia, Hungary, Italy, etc., the soils about old village sites contain relatively large quantities of potassium nitrate. These alkalies occur in various silicate and alumino-silicate minerals. The more important are the potash felspars, micas, leucite, glauconites, and alunites. Potassium is usually accompanied by sodium. The analyses indicated in Table I illustrate the composition of these minerals.

TABLE I.—ANALYSES OF SILICATE MINERALS.

	Potash felspar.	Leucite.	Muscovite.	Glauconite.	Alunite (pink).	Alunite (white)
Silica, SiO_2	64·98	50·23	54·00	46·58	1·92	19·34
Titanic oxide, TiO_2	nil	2·27	1·51	—	—	—
Alumina, Al_2O_3	19·18	11·22	26·23	11·45	37·52	37·37
Ferric oxide, Fe_2O_3	0·33	5·34	3·81	22·00	0·26	0·27
Lime, CaO	0·20	5·99	0·52	2·49	—	—
Magnesia, MgO	0·25	7·09	0·83	1·27	—	—
Potash, K_2O	12·79	9·81	4·41	6·96	9·51	5·68
Soda, Na_2O	2·32	1·37	4·00	0·98	1·12	1·08
Loss on ignition	0·48	2·65	4·31	9·66	13·19	13·86
Sulphur trioxide, SO_3	—	—	—	—	36·76	22·09

Clays contain from about half to five per cent. In British fireclays, the amount of potash, K_2O, is commonly from three to four times the amount of soda, Na_2O.

Nearly all silicates contain some sodium, and there are several silicates which contain relatively large quantities—*e.g.* soda felspar or albite; the soda-lime felspars —*e.g.* labradorite; sodalite; nepheline; analcime; lapis lazuli; etc.

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	Water
Albite . . .	67·70	20·99	0·21	0·14	0·22	0·54	10·65	0·47
Nepheline . .	37·22	28·32	0·51	0·07	4·40	0·18	19·43	4·07
Sodalite . .	37·96	30·96	0·85	—	0·46	0·74	22·93	1·10

This nepheline also contained 6·12 per cent. of carbon dioxide, and the sodalite 5·34 per cent. of chlorine. Sodium is also found in limestones, dolomites, asbestos, talc, ironstones, and various other minerals—*vide* sodium carbonate.

The alkaline lakes of Nevada and South California give sodium carbonate on evaporation. "Natural soda," also called after the Egyptian term *trona*, or the Mexican term *urao*, has been extracted commercially at Owen's lake. Trona from that district has a composition corresponding with $Na_2CO_3.NaHCO_3.2H_2O$. These alkalies also occur in soils whence they have been derived from the weathering and decomposition of rocks. Only a fractional part of the total alkali is in the soluble form, and accessible to plants as food. The soluble potash salts are selectively absorbed and retained by soils the soluble sodium salts are scarcely absorbed at all.[2] In consequence, soluble sodium salts are much more readily leached from soils (and clays) than soluble potassium salts. The soluble portion of a soil normally contains more potassium than sodium salts, since the latter will have been leached away by percolating water. In illustration, the soluble matter of 12 soils picked at random contained from 4 to 6 times more potassium than sodium salts. The potash salts are an important constituent of plant food; all fruitful soils contain soluble potash salts. Plants also preferentially absorb potash salts, and this is equally true of marine and land plants. In the absence of potash, the plant cannot assimilate the sodium, rubidium, or cæsium salts.[3] In fact, lithium, potassium, cæsium, and rubidium salts seem to act on vegetable life as poisons in the absence of sodium salts. The ashes of plants thus contain potassium combined with the constituents of the plant in some form, and this compound is decomposed largely into potassium carbonate on ignition. Much of the sodium in plant ashes is in an insoluble form, and has in some cases thus escaped recognition. While the potash *salts in plants are confined to certain organs, the sodium salts appear to be uniformly* diffused through the whole organism. Seaweeds, and plants grown near the sea, contain salts, and the ashes of such plants may or may not contain more soda than potash. H. L. Duhamel du Monceau[4] sought to find if the difference in the proportion of the two alkalies in the ashes of plants is a characteristic of the plant itself, or due to the nature of the soil on which it grows; and with the aid of L. C. Cadet, he was able to prove that when the plant *salsola* grows near the sea, the ash contains much soda; but if grown further inland, the ash gradually gains in potash, and loses in soda; and B. Corenwinder showed that the reverse obtains when inland plants are grown nearer the sea. The ash of many seaweeds, however, contains more potash than soda. Before the advent of the Stassfurt salts, the preparation of potash salts from the ashes of seaweeds was a flourishing industry in Scotland, which dated back to 1730. The soluble salts in the ash of the seaweed collected on the west coast of Scotland contained about 30 per cent. of potassium salts and 12 per cent. of sodium salts; that collected on the west coast of Ireland contained about 38 per cent. of potassium salts and 17 of sodium salts.

B. Palissy, in his *Traité des sels divers et du sel commun* (Paris, 1580), showed that the ash of the bark of trees is richer than the inner wood in alkaline salts. In illustration, the bark of the oak has 0·42 per cent. potash, K_2O, the wood 0·15 per cent. Similarly, for the beech—bark 0·15, wood 0·06 per cent.; for the maple—bark 0·67, wood —0·12; spruce—bark 0·12, wood 0·04. These numbers also show how large a quantity of wood would be needed for the production of considerable quantities of potassium carbonate. If all the contained potash could be

recovered from the ash, a ton of anhydrous potassium carbonate would require from 400 to 500 tons of wood. Some plants have larger amounts of potash than wood—*e.g.* thistles and vines about 0·5 per cent., ferns about 0·6 per cent.; nettles have 2·7 per cent.; wormwood, 7·3 per cent.

The potash which many herbivorous animals draw from the plants on which they feed is excreted from the skin as sweat. With sheep, the potash is largely retained in the wool in a form called *suint* or *wool fat*. The suint furnishes the eq. of about 5 per cent. of potassium carbonate, calculated on the total weight of the wool. Most parts of animal bodies and animal fluids contain sodium chloride; and when ignited furnish an ash which contains 5 to 75 per cent. of sodium chloride. Lithium, sodium, potassium, rubidium, and cæsium have all been reported in solar spectra.[5] Lithium, rubidium, and cæsium are widely diffused in nature, but in rather small quantities. They have all been reported as constituents of certain mineral springs.[6] G. Kirchhoff and R. Bunsen found 0·0391 grm. of lithium chloride, 0·00021 grm. of rubidium chloride, and 0·00017 grm. of cæsium chloride in a litre of the mineral water of Dürkheim. The waters of Aachen, Assmannshausen, Baden-Baden, Bad-Orb, Biling Ems, Egger-Franzenbad, Homberg, Karlsbad, Kissingen, Kreuznach, Marienbad, Salsomaggiore, Salzschlirf, Sciacca, Selters, Tarasp, Wheel Clifford, and Wildbad have been reported to contain lithium; those of Aussée, Bourbonne-les-Bains, Hall, Haute Marne, Kissingen, Ems, Kochbrunnen, Nauheim, Selters, Theodorshall, Ungernach, Vichy, and Wildbad to contain rubidium; and those of Aussée, Baden-Baden, Bourbonne-les-Bains, Ems, Frankenhausen, Hall, Kreuznacher, Monte Catino, Monte Doré, Hauheim, Vichy, and Wheal Clifford to contain cæsium. These elements have also been reported in the ashes of many plants—*e.g.* tobacco. Lithium has been reported in the ash of seaweed, cocoa, coffee, sugar cane, etc.; rubidium in the ashes of beet-root, coffee, tea, oak, and beech; in crude tartar, and in the mother liquid from the extraction of the Stassfurt salts. Lithium has also been reported in milk, human blood, and muscular tissue; and in meteorites, soils, and sea water. L. de Luise found lithium in some salts of Vesuvian fumaroles.

Lithium occurs in small quantities in a great many minerals. L. Dieulafait[7] has given a list of about 140 minerals containing this element. Spodumene, lepidolite, triphylite, lithiophylite, amblygonite, natroamblygonite, petalite, and sickerlite are the most important sources of this element.

Petalite is an aluminosilicate approximating $LiAl(Si_2O_5)_2$; it usually contains 2 to 5 per cent. of lithia, Li_2O. The monoclinic crystals are rare; it usually occurs in foliated masses, white-tinged red or grey. Sp. gr., 2·5; hardness, 6. It is not attacked by acids. **Spodumene** or **triphane** is another aluminosilicate approximating $LiAl(SiO_3)_2$; and containing from 4 to 8 per cent. of lithia. It occurs in monoclinic prisms, and also massive. Its colour may be white, grey, green, yellowish-green, or blue. Sp. gr., 3·0; hardness, 7. It is not attacked by acids. There are two gem-varieties—*hiddenite*, which is yellowish-green or emerald-green; and *kunzite*. **Eucryptite** is an aluminosilicate approximating $LiAlSiO_4$, which contains from 2 to 10 per cent. of lithia. It occurs in hexagonal crystals, white and transparent. The sp. gr. is 2·6. The average values of some analyses are as follows:

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Li_2O
Petalite . . .	77·62	16·66	0·20	—	—	0·21	1·45	3·42
Spodumene . .	63·65	26·24	1·36	0·48	1·01	0·72	0·77	6·05
Eucryptite . .	48·46	40·50	0·02	—	—	0·47	—	10·90

There are several varieties of mica which contain this element; **lepidolite,** one of the simplest, has the type-formula $R_3Al(SiO_3)_3$, and it contains from 4 to 6 per cent. of lithia. It occurs in scaly masses, the crystals are monoclinic; red, violet, grey, yellow, or white in colour; sp. gr., 2·8; hardness, 2·5. After calcination, it is decomposed by hydrochloric acid with the separation of gelatinous silica. A variety found in pegmatite veins (Wisconsin) is called *irvingite;* another rather

more complex mica with about 2·5 per cent. of lithia is called *cookeite*. Another complex lithia mica called **zinnwaldite** occurs in the tin deposits of Zinnwald and Erzgebirge. Its analysis approximates to $(K_2Li)_3FeAl_3Si_5O_{16}(OH_3F)$, and it contains 3 to 4 per cent. of lithia, and it crystallizes in the monoclinic system; the colour may be violet, yellow, brown, or grey; its sp. gr. is 3·0; and its hardness 2·5. An emerald-green variety with 4 to 5 per cent. of lithia, called *cryophylite*, comes from Massachusetts; and a dark grey ferruginous variety with about 3 per cent. of lithia and sp. gr. 3·14 to 3·19, called *rubenglimmer*, comes from Saxony. The average values of some analyses are as follows:

	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	Li_2O	H_2O	F
Lepidolite . . .	50·61	25·13	0·42	12·27	1·08	4·88	1·56	—
Zinnwaldite . .	49·02	19·36	8·75	11·85	0·44	4·13	1·68	7·36

A number of complex phosphatic minerals contain up to 10 per cent. of lithia. **Triphylite** forms rhombic crystals of a greenish or bluish-grey colour—if the colour is yellowish-brown or salmon, the mineral is called **lithiophylite.** Its composition approximates $4(Fe_2Mn)PO_4$, with 8 to 9 per cent. of lithia; sp. gr., 3·5; hardness, 4·5; and it is soluble in hydrochloric acid. The mineral alters by weathering, etc., forming what are called *heterosite*, *pseudotriplite*, *aluandite*, and *natrophylite*, which also contain more or less lithia. **Amblygonite** is a fluorophosphate, approximating $Li(AlF)PO_4$, with 8 to 9 per cent. of lithia. It occurs in triclinic crystals coloured white, yellow, grey, brown, or green. Its sp. gr. is 3·0; hardness, 6. The powdered mineral dissolves in dil. sulphuric acid. *Natroamblygonite*, corresponding with $NaAl(OH)PO_4$, usually has 3 to 4 per cent. of lithia. A more complex mineral called *sicklerite* contains 3 to 4 per cent. of lithia. The average values of some analyses:

	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	Li_2O	H_2O	P_2O_5
Triphylite . .	—	40·23	0·10	0·83	0·26	8·15	0·87	43·18
Lithiophylite . .	—	14·44	—	—	0·29	9·26	0·17	45·22
Amblygonite . .	33·79	—	—	—	1·88	1·83	4·18	47·94

The lithiophylite had also about 32 per cent. and the triphylite about 9 per cent. of manganese oxide, MnO. All the minerals have about one per cent. of insoluble earthy gangue.

A mineral called *cryophylite*, from Massachusetts, is an impure lithia cryolite, $3(Li,Na)F.AlF_3$, or $3LiF.3NaF.2AlF_3$. It contains 5 to 6 per cent. of lithia. A red or pink gem variety of tourmaline called *rubellite* contains lithia. Small quantities of lithia have also been reported in beryl, leucite, lepidomelane, anorthite, enstatite, biotite, muscovite, phenacite, psilomelane, heulandite, epidote, scapolite, phlogopite, pinite, cryolite, orthoclase, richterite, basalt, etc. Rubidium and cæsium occur in many of the lithia minerals—*e.g.* lepidolite may contain up to 3 per cent. of rubidia and 0·7 per cent. of cæsia; beryl has been reported with up to 3 per cent. cæsia. Traces of these elements have been reported in carnallite, leucite, mica, orthoclase, lithiophylite, triphylite, spodumene, leucite, etc. The very rare mineral **rhodizite,** found in minute crystals—cubic system—on tourmaline in the Urals, is regarded as an aluminoborate of cæsium, rubidium, and potassium approximating $R_2O.2Al_2O_3.3B_2O_3$, where the alkali bases, R_2O, aggregate about 12 per cent. Its crystals resemble those of boracite. Its sp. gr. is 3·4; hardness, 8. The mineral **pollux,** or **pollucite,** is regarded as a hydrated cæsium sodium aluminium silicate.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	Cs_2O	H_2O
Elba . .	44·03	15·97	0·68	0·68	3·88	34·07	2·40
Hebron . .	43·48	16·41	—	0·21	1·72	36·77	1·53

It has 30–36 per cent. of cæsia, it forms colourless cubic crystals; sp. gr., 2·9; hardness, 6·5. Small quantities of pollucite occur in the granites of Elba; and at Hebron (Maine). The sample of pollucite from Hebron (Maine) also contained 0·47 per cent. of K_2O; and 0·03 per cent. of Li_2O.

In connection with cæsium, it is interesting to note that C. F. Plattner, in 1845, was not able to make his analysis of the mineral *pollux* (from Elba) add up to 100 per cent., and he sought in vain for the missing element. In spite of adverse criticism, C. F. Plattner [8] insisted upon the general accuracy of his work, although it must have demanded some self-control to publish the results. A man imbued with less faith in his work would have suppressed the results as absurd. Not so Plattner. He waited. After R. Bunsen and G. Kirchhoff had discovered cæsium, F. Pisani (1864) showed that C. F. Plattner had mistaken cæsium (at. wt. 132·8) for potassium (at. wt. 39·11). By making the corresponding correction, Plattner's analysis was found to be quite satisfactory.

To make this quite clear, suppose that 5 grms. of a compound, supposed to be potassium chloride, are obtained. This will be multiplied by 0·631 to get the eq. amount, 3·16 grms. of K_2O; but if the compound be CsCl, not KCl, then the weight must be multiplied by 0·835 to get the corresponding amount, 4·18 grms. of Cs_2O. The analysis would thus appear to be 4·18 less 3·16, that is 1·02 grms. too low if the 5 grms. of cæsium chloride were mistaken for potassium chloride. This is a remarkable tribute to the accuracy of Plattner's analysis.

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§ 3. The Potash Salt Beds

In the thirteenth century, and earlier, the salt or brine springs—called *sool*—near Stassfurt furnished the surrounding country with a certain amount of salt—sodium chloride. The first sool wells were built there in 1452, and in his *De ortu et causis subterraneorum* (Basil, 1546), G. Agricola expressed the opinion that these springs must have their origin in underground layers of salt; but the remark passed unheeded until the supplies from the salt springs had become inadequate for the needs of Prussia. In 1838, C. J. B. Karsten [1] reported that sool springs no doubt obtained their salt from rich subterranean saline beds which would probably be reached by making deep borings in the vicinity of the brine wells. Accordingly, a boring was started in 1839 in the hope of finding deposits of rock salt of a good quality. When the saline bed was reached in 1843, at a

depth of about 768 feet, the salt was found to be a mixture of magnesium and potassium compounds; and from later borings, the existence of compact layers of rock salt was demonstrated; but "unfortunately," said B. von Cotta,[2] "the Stassfurt rock salt appears to be mixed with much magnesium and potassium salts and boracite"; and the question was discussed whether it was really worth while to risk the great expense in working a shaft in order to mine this "by no means pure salt."

Borings show that the deposits underlie the country around Stassfurt, near the Harz mountains, in Prussian Saxony, over an area of about 100 sq. miles, and extend from Mecklenberg in the north, to Thuringia in the south, and Hannover in the west.[3] A commencement in shaft sinking was made in 1851, and rock salt was mined. The overburden of potassium and magnesium salts had to be cleared in order to reach the rock salt. These salts were at first rejected as worthless, and they were called **Abraumsalze**—*Abraum*, refuse; *Salze*, salts. A little while before this, J. von Liebig had emphasized the facts (i) that potash is a necessity for the normal nourishment of plants; (ii) that potash is extracted by plants from the soil; and (iii) that if the soil is to remain fruitful, the supply of potash must be continually replenished. The agriculturists' demand for potash as a fertilizer directed attention to the waste salts, which were soon recognized to be a valuable source of potassium and magnesium. Processes were soon devised for the extraction of potassium and magnesium salts from the refuse salts, with the result that the rock salt, originally sought, became of secondary importance—a by-product in fact—and the original refuse, once thought to spoil the brine, assumed prime importance.

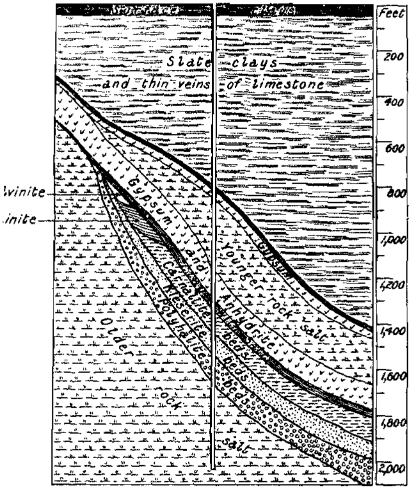

FIG. 1.—Section of Shaft in the "Ludwig II" Potash Mine at Stassfurt.

A. Frank erected the first works for the extraction of potassium chloride in 1861, and an important industry, controlled by the *Verkaufs-Syndikat der Kaliwerke* (Leopoldshall, Stassfurt), has been established. Up to 1914, the agricultural world was almost wholly dependent on the German mines for its supply of potash, and was virtually under the control of the German syndicate. As a result of the 1914–1919 war, instigated by Germany, the Alsace deposits passed into the hands of the French. The output of crude salts from the mines in 1861 was 2293 metric tons, and in 1900, 3,037,035 metric tons. The output for the Stassfurt mines, in 1913, was equivalent to 1,110,000 tons of K_2O, and about half of this was used in Germany; United States took most of the remainder; Great Britain imported about 32,000 tons.[4] The consumption of potash salts compiled from German official sources, 1910–17, is as follows. The "foreign" consumption from 1914 was, of course, diminished on account of the Allies' blockade of Germany. In

1919, 946,000 short tons were produced, 264,000 were sold abroad, and the remainder satisfied about 41 per cent. of home requirements.

Year.	Domestic sales, tons.	Foreign sales, tons.	Total sales, tons.	Percent. used in agriculture.	Percent. used in industry.
1910	460,618	346,473	807,091	88·3	11·7
1911	527,822	441,941	969,763	90·5	9·5
1912	581,422	524,514	1,105,936	89·5	10·5
1913	664,711	556,695	1,221,406	90·4	9·6
1914	591,590	402,797	994,387	91·2	8·8
1915	623,807	123,947	747,754	92·0	8·0
1916	797,548	174,825	972,373	94·1	5·9
1917	958,625	146,084	1,104,709	95·7	4·3

The consumption of potash, K_2O, in agriculture during 1913 in Germany was 589,713 tons; Belgium, 14,501; Holland, 47,826; France, 36,426; United Kingdom, 25,572; Luxemburg, 442; Austria, 23,072; Hungary, 4508; Switzerland, 3639; Italy, 6990; Russia, 24,920; Spain, 9122; Portugal, 1365; Sweden, 21,465; Norway, 3953; Denmark, 8222; Finland, 1766; Balkan States, 218; Asia, 6281; Africa, 4807; United States, 254,859; Canada, 1513; the remainder of North and South America, 10,140; and Australia, 2739.

Other potash deposits.—In 1904, J. Vogt and J. B. Grisez discovered potash deposits in Upper Rhine while some borings were being made at Wittelsheim in Alsace in quest of coal.[5] The deposit is composed of two layers separated by a band of rock salt about 60 ft. thick, and it is reported that the bed occurs in the plain bounded by the Jura on the south, by the Vosges on the west, and on the east by the Rhine, and to extend as far as the suburbs of Mulhausen. The secondary beds of the same formation stretch across the Rhine into Baden. The lower more important bed occurs at a depth between 650 and 1000 metres, it is on the average 4 metres thick, and occupies an area of 200 sq. kilometres; the upper less important bed lies 15 to 25 metres above the other bed. Both beds are nearly horizontal and, for the most part, contain sylvinite, and above them is a bed of rock salt 250 metres thick. The upper bed averages 30 per cent. KCl, the lower one 35 per cent. KCl. The whole deposit contains about 15,000,000,000 tons of material with an average of 22 per cent. K_2O, or the whole deposit contains over 300 million tons of K_2O. There is also a deposit of less importance in Austrian Galicia.[6] The beds have been worked some years, but are not sufficient to provide for Austria-Hungary, since that country imported 21,000 tons from Germany in 1913. Important deposits were found, in 1912, at Suria, in the salt district of Cardona (Catalonia) in Spain, and they have been described in a pamphlet *Sales Potasicas en Cataluna* (Madrid, 1914).[7] Some samples of caliche in the Chilean nitre beds contain appreciable quantities of potassium nitrate.[8] A small quantity of potash has been obtained from mines in Kheura (Punjab) in India.[9] There is a deposit in a recent lacustrine formation at Eritrea (Somaliland). The reserve is small, but the deposit is rich 80 per cent. potassium chloride. In Chile, in the Lakes Pintados and Bella Vista, in the provinces of Atacama and Tarapaca, there are deposits with from 3 to 36 per cent. of chloride; the reserves are estimated at two million tons. There are also undeveloped deposits in Peru, Russia, Morocco, Overyssel (Holland). In Brazil there is said to be a deposit with 89 per cent. potassium nitrate.[10]

The brines of the Lonar Lake, Buldana district, India,[11] are said to contain 0·1 per cent. of potash calculated on the soluble salts. In Tunis, south of Gabes, there is a salt-lake worked since 1915, primarily for bromine; a crude potassium chloride—40 per cent. K_2O—called *sebkainite*, is obtained by solar evaporation and crystallization. In 1917, 20,000 tons were produced. The brines of several alkali lakes and ponds in Western Nebraska contain appreciable quantities of potash—the brine is reported to contain the eq. of about 3 per cent. of potash (K_2O), and

the solid residue eq. of 15 per cent. K_2CO_3, and 33 per cent. of K_2SO_4. It is also suspected that potash deposits in dried-up lake beds will be located in the vicinity of Magum (Oklahoma).[12] J. W. Turrentine has compiled analyses of 168 samples of the brines of the United States, and the percentage K_2O in the solid residues ranged from 0·89 to 12·19 per cent. The deposits about Stassfurt, however, are so large compared with all other sources of supply that up to the arrest of supplies in 1914, the Germans have had practically a monopoly of the potash trade of the world.

The composition of the Stassfurt salt beds.—The deposits about Stassfurt *may very roughly be grouped in a series of strata indicated in Fig. 1.*[13] Starting from a basal layer of anhydrite and gypsum there are :

(1) ***Rock salt bed.***—An immense basal bed of *alteres Steinsalz*—older rock salt—broken up at fairly regular intervals with two- to five-inch bands of anhydrite, $CaSO_4$.

(2) ***Polyhalite bed.***—Above the basal salt is a layer of rock salt, sometimes 200 feet thick, mixed with 6 or 7 per cent. of *polyhalite*, $2CaSO_4.MgSO_4.K_2SO_4.2H_2O$, anhydrite, *and magnesium chloride. An average analysis shows : 91·2 per cent. of sodium chloride ;* 6·6 per cent. of polyhalite ; 1·5 per cent. of *bischofite*, $MgCl_2.6H_2O$; and 0·7 per cent. of anhydrite.

(3) ***Kieserite bed.***—Resting on the polyhalite bed is a layer of rock salt, sometimes 100 feet thick, mixed with layers of *kieserite*, $MgSO_4.H_2O$, and other sulphates, approximating on the average 65 per cent. of rock salt ; 17 per cent. of kieserite ; 13 per cent. of *carnallite*, $KCl.MgCl_2.6H_2O$; 3 per cent. of bischofite ; and 2 per cent. of anhydrite.

(4) ***Carnallite bed.***—*Finally comes a reddish layer of rock salt associated with various* salts of magnesium and potassinm approximating on the average 55 per cent. of carnallite ; 25 per cent. of rock salt ; 16 per cent. of kieserite ; and 4 per cent. of other salts—chiefly bischofite, *tachhydrite*, $2MgCl_2.CaCl_2.6H_2O$; *astracanite*, $MgSO_4.Na_2SO_4.4H_2O$; *schönite*, $MgSO_4.K_2SO_4.6H_2O$; and *boracite*, $MgCl_2.2Mg_3B_8O_{15}$.

The more soluble salts usually predominate in the upper layers, while anhydrite and the less soluble salts accumulate in the lower layers. These four beds are capped by a layer of grey salt clay—*Salzthon*—followed by layers of gypsum, $CaSO_4.2H_2O$, and anhydrite, $CaSO_4$; *jungeres Steinsalz*—younger rock salt ; bunter clay shales ; and finally surface drift or soil. Over thirty saline minerals have been reported in the Stassfurt deposits—some occur sparingly, others abundantly ; those marked with an asterisk are the most important :

Halite (or rock salt) *	$NaCl$
Sylvine (or sylvite) *	KCl
Douglasite	$2KCl.FeCl_2.2H_2O$ (?)
Bischofite	$MgCl_2.6H_2O$
Tachhydrite	$2MgCl_2.CaCl_2.12H_2O$
Carnallite *	$MgCl_2.KCl.6H_2O$
Thenardite	Na_2SO_4
Glauberite	$Na_2SO_4.10H_2O$
Kieserite *	$MgSO_4.H_2O$
Leonite (or potassium astracanite)	$MgSO_4.K_2SO_4.4H_2O$
Astracanite (or bloedite)	$MgSO_4.Na_2SO_4.4H_2O$
Schönite (or picromerite)	$MgSO_4.K_2SO_4.6H_2O$
Epsomite (or richardite)	$MgSO_4.7H_2O$
Kainite *	$MgSO_4.KCl.3H_2O$
Polyhalite *	$MgSO_4.K_2SO_4.2CaSO_4.2H_2O$
Langbeinite	$2MgSO_4.K_2SO_4$
Krugite	$MgSO_4.K_2SO_4.4CaSO_4.2H_2O$
Vanthoffite	$MgSO_4.3Na_2SO_4$
Löwite	$MgSO_4.Na_2SO_4.2\frac{1}{2}H_2O$
Anhydrite (or karstenite)	$CaSO_4$
Gypsum	$CaSO_4.2H_2O$
Glaserite (or aphthitalite)	$3K_2SO_4.Na_2SO_4$
Boracite (or stassfurtite) *	$2Mg_3B_8O_{15}.MgCl_2$
Sulphoborite	$Mg_6H_4O_{12}(SO_4)_2.7H_2O$; or $2MgSO_4.4MgHBO_3.7H_2O$
Pinnoite	$MgB_2O_4.3H_2O$
Ascharite	$MgHBO_3$; or $3Mg_2B_2O_5.2H_2O$
Heintzite	$Mg_4K_2B_{22}O_{38}.14H_2O$
Hydroboracite	$MgCaB_6O_{11}.6H_2O$ (?)

The different minerals can rarely be distinguished by mere inspection. The nature of the products of the mines is largely established by chemical analysis. The average composition of the crude natural kainite, carnallite, rock kieserite, and sylvinite is indicated in Table II.

TABLE II.—ANALYSES OF THE CHIEF RAW PRODUCTS OF THE STASSFURT MINES.

Constituent.	Kainite.	Carnallite.	Kieserite.	Sylvinite.	Potash.	Manure salts.
Potassium sulphate, K_2SO_4	21·3	—	—	1·5	2·0	1·2
Potassium chloride, KCl .	2·0	15·5	11·18	26·3	31·6	47·6
Magnesium sulphate, $MgSO_4$	14·5	12·1	21·5	2·4	10·6	0·4
Magnesium chloride, $MgCl_2$	12·4	21·5	17·2	2·6	5·3	4·8
Sodium chloride, NaCl .	34·6	22·4	26·7	56·7	40·2	26·2
Calcium sulphate, $CaSO_4$.	1·7	1·9	0·8	2·8	2·1	2·2
Insoluble in water . .	0·8	0·5	1·3	3·2	4·0	3·5
Water, H_2O . . .	12·7	26·1	20·7	4·5	4·2	5·1
Average K_2O . .	12·8	9·18	7·5	17·4	21·0	30·6
Guaranteed minimum K_2O	12·4	9·0	—	12·4	20·0	30·0

The strata in different localities do not always follow the same regular order since local conditions and geological disturbances have produced some alterations—*e.g.* surface water may have entered and washed away the potash salts or modified the strata in other ways. Carbonates are very scarce. There is some bituminous limestone—*stinkstone*—below the basal anhydrite. The saliferous clay, the rock salt, and the carnallite contain traces of sulphur which has been formed by the reduction of gypsum by organic matters; some pyrites is also present. F. Bischof [14] found traces of bromine, cæsium, and rubidium in the Stassfurt rock salt, but he could detect neither iodine nor lithium; J. N. von Fuchs reported traces of iodine in the rock salt of Hall (Tyrol). A. Vogel [15] found ammonium chloride to occur in the rock salt of Friedrichshall (Würtemberg), and other localities; celestine, $SrSO_4$, and nitrates have been reported in the deposits. The term *sylvinite* has been applied to a mixture of potassium and sodium chlorides; and *Hartsalz*—hard salt—to a dark reddish-brown mixture of sylvinite and kieserite with some anhydrite. The two terms sylvinite and hard salt are employed rather indefinitely; hard salt has nearly the same ultimate composition as kainite, and sylvinite is not unlike hard salt, but it contains rather more potash. The chlorides—*koenenite*, $Al_2O_3.3MgO.2MgCl_2.6(\text{or } 8)H_2O$, and *bæumlerite*, $KCl.CaCl_2$—and the sulphate—*syngenite*, $CaK_2(SO_4)_2.H_2O$—have been reported in some other potash deposits, but not in those of Stassfurt.

The Stassfurt deposits have been the subject of elaborate investigations by J. H. van't Hoff and his school.[16] In 1849, J. Usiglio [17] studied the deposition of salts when sea water is conc. by evaporation, and examined the residues analytically. He found that calcium carbonate was first eliminated, then calcium sulphate, then sodium chloride, and the more soluble salts accumulated in the mother liquid. This method of investigation does not allow sufficient time for the various salts to attain a state of equilibrium, and it therefore follows that the natural evaporation of brines probably furnishes somewhat different results. Moreover, it is difficult, if not impossible, to identify the several substances which separate from the mother liquid formed during the later stages of the evaporation. J. H. van't Hoff followed the synthetic method in his study of this subject. He started from simple soln. like those of sodium and potassium chlorides, under definite conditions of temp., and gradually added the pertinent constituents until the subject became so complicated that the crystallization of the constituents from concentrating sea water was reduced to a special case of a far more comprehensive work.

The crystallisation of salts from mixed solutions.—The simple cases of the

crystallization of soln. sat. with but one salt, and of soln. of two salts which do not react with one another, nor form hydrates, have been discussed. The phenomenon is more complex when the salts present in the soln. form a series of hydrates, or when the salts can react with one another to form double salts.

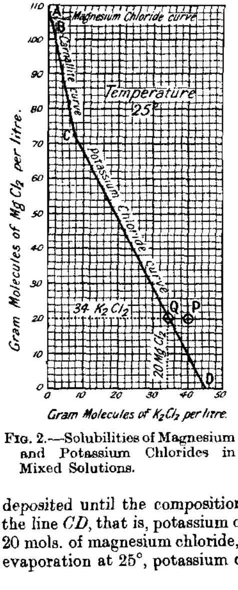

FIG. 2.—Solubilities of Magnesium and Potassium Chlorides in Mixed Solutions.

A soln. of potassium and magnesium chlorides not only furnishes crystals of magnesium chloride, $MgCl_2.6H_2O$, and of potassium chloride, KCl, but also crystals of the double salt carnallite, $MgCl_2.KCl.6H_2O$. Referring to Fig. 2, the line AB represents the effect of additions of potassium chloride on the amount of magnesium chloride required to form a sat. soln. at 25°. The solubilities are here expressed in terms of the number of mols. of $MgCl_2$ and of $(KCl)_2$ per 1000 c.c. The symbol $(KCl)_2$ is not intended to imply that the molecule of this salt is K_2Cl_2, but is simply used to keep the molecules of magnesium and potassium chlorides eq. as units for the ordinates and abscissæ in the diagram. The line BC represents the amount of carnallite in a sat. soln. as the amount of potassium chloride is increased; and the line CD represents the amount of potassium chloride in a sat. soln. as the amount of magnesium chloride is increased. All soln. represented by points on the line $ABCD$ are sat. with one of these salts. If, therefore, we could start with a soln. containing, say, 20 mols. of magnesium chloride, and 40 mols. of K_2Cl_2 per litre, at the constant temp. 25°, the composition of the soln. would be represented by the point P on the diagram. Crystals of potassium chloride would be deposited until the composition of the soln. could be represented by a point Q on the line CD, that is, potassium chloride would be deposited until the soln. contained 20 mols. of magnesium chloride, and 34 of K_2Cl_2 per litre. If the soln. were conc. by evaporation at 25°, potassium chloride would continue separating until the conc. of the soln. could be represented by a point C; that is, until the soln. contained about 5·5 mols. of K_2Cl_2, and 72·5 mols. of $MgCl_2$ per litre. If the mother liquor were to be still further conc. at 25°, crystals of carnallite and of potassium chloride would separate until the conc. of the soln. could be represented by a point B, corresponding with one mol. of K_2Cl_2 and 105 mols. of $MgCl_2$. Any further conc. of the mother liquid would lead to the separation of magnesium chloride and carnallite in constant proportions until the soln. dried.

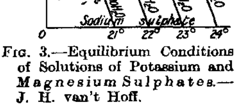

FIG. 3.—Equilibrium Conditions of Solutions of Potassium and Magnesium Sulphates.—J. H. van't Hoff.

The equilibrium curve of mixtures of sodium and magnesium sulphates in aq. soln. for temp. up to just over 100°, is represented by Fig. 3. Below 22°, the case is analogous with mixtures of sodium and potassium chlorides, Fig. 1 (1. 11, 1), for sodium or magnesium sulphate alone crystallizes from the soln. as illustrated by the set of curves A_1; at 22° A_2, the double salt astracanite appears, and at higher temp., the zone of stability of astracanite widens as shown by the portions of the curves A_3 and A_4 between the dotted lines of the diagram. No astracanite separates from a sat. soln. of the two sulphates if the temp. is below 22°,

showing that if this double salt occurs in a deposit, its existence is evidence that the *temp. of its formation must have exceeded 22°. This temp., 22°, marking the limit* of stability of astracanite, may be altered by the presence of other salts in the soln. Certain salts which separate from a crystallizing soln. when the evaporation is conducted at one temp., may not appear if the evaporation be conducted at a higher temp., thus, epsomite, $MgSO_4.7H_2O$, does not occur over 47°, schönite over 47·5°, carnallite over 167·5°, and tachhydrite over 83°. Analogous observations have been observed in natural evaporations; thus, R. Brauns [18] reports that in summer, on the shores of the Caspian Sea, gypsum, magnesium sulphate, and rock salt separate from the brine, whereas in winter, Glauber's salt, $Na_2SO_4.10H_2O$, or thenardite, Na_2SO_4, is formed; and in spring and autumn, rock salt and astracanite, $Na_2SO_4.MgSO_4.4H_2O$, appear. According to J. H. van't Hoff, glauberite is formed below 10°; langbeinite, above 27°; löwite, above 43°; vanthoffite, above 46°; löwite with glaserite, over 57°; löwite with vanthoffite, over 60°; kieserite *with sylvite, above 72°; and kainite with sylvite, up to 83°. A scale of temp. of* this kind is regarded as a kind of *geologische Thermometer.*

Equilibrium conditions in solutions of potassium and magnesium chlorides.—The equilibrium diagram of soln. of magnesium and potassium chlorides has been studied by J. H. van't Hoff and W. Meyerhoffer.[19] The variation of the range of stability of the different phases up to about 185° are illustrated in Fig. 4. The surface areas represent soln. sat. with the phases named; the lines represent soln. sat. with the salts indicated in the adjoining areas; points below the surface of the solid figure represent unsaturated soln.; and points outside the solid figure represent supersaturated soln. The composition corresponding with a point on the surface of the figure is obtained by measuring the vertical distance of the point from the $MgCl_2$ and the K_2Cl_2 planes; and the corresponding temp. by its vertical distance to the right or left of a plane passing through 0°, and perpendicular to the K_2Cl_2- and the $MgCl_2$-planes. For example, the point P corresponds with a soln. containing 166·7 mols. of KCl, per 1000 mols. of water—melting temp. of carnallite 167·5°. The curve AP represents the solubility curve of carnallite in the presence of an excess of potassium chloride. The point numbered 116·67 represents the transition of $MgCl_2.6H_2O$ into $MgCl_2.4H_2O$; and that marked 115·7°, the transition temp. in the presence of carnallite. In an analogous way, the point marked −33·6° represents the cryohydric temp. between $MgCl_2.12H_2O$ and ice, and −34·3° the cryohydric temp. of $MgCl_2.12H_2O$ and ice in the presence of potassium chloride. Otherwise the diagram explains itself.

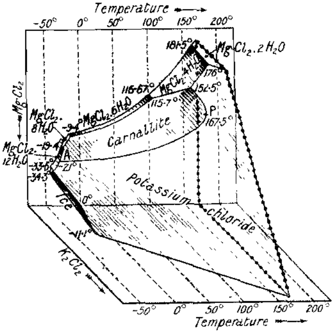

FIG. 4.—Equilibrium Conditions of Solutions of Magnesium and Potassium Chlorides—J. H. van't Hoff and W. Meyerhoffer.

Equilibrium conditions in solutions of potassium and magnesium sulphates.—The equilibrium conditions with soln. of magnesium and potassium sulphates, at different temp., are illustrated by the diagram, Fig. 5. The point A represents the f.p. of water, 0°; B, the cryohydric temp., −2·9° for magnesium sulphate; C, the cryohydric temp., −1·5°, for potassium sulphate; D, the cryohydric temp., −4·5°, for the mixed potassium sulphate and schönite; E, the cryohydric temp., −5°, for the mixture of schönite and $MgSO_4.12H_2O$; F, the transition point, 0·7°, for the

conversion of $MgSO_4.12H_2O$ into $MgSO_4.7H_2O$ in the presence of schönite; and *G*, the eutectic temp., $-1·8°$, for the mixture $MgSO_4.12H_2O$ and $MgSO_4.7H_2O$. Surface areas represent soln. sat. with the phases indicated thereon; lines represent soln. sat. with the substances indicated on the adjoining areas. The triple and quadruple points have the usual significations. Points within the surface areas of the diagram represent sat. soln.; points below the surface areas represent unsaturated soln.; and points outside, supersaturated soln.

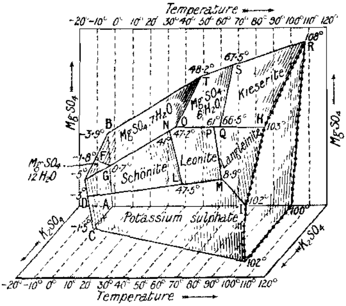

FIG. 5.—Equilibrium Conditions of Solutions of Magnesium and Sodium Chlorides—J. H. van't Hoff and W. Meyerhoffer.

Equilibrium conditions in solution of potassium and magnesium chlorides and sulphates.—Similar principles obtain with still more complicated examples, say, a mixture of potassium chloride and magnesium sulphate, where there is a reaction: $2KCl + MgSO_4 = MgCl_2 + K_2SO_4$. Such a soln. may lead to the separation of crystals of potassium chloride and potassium sulphate; magnesium chloride; two hydrates of magnesium sulphate, *viz.* $MgSO_4.7H_2O$, and $MgSO_4.6H_2O$; carnallite, $MgCl_2.KCl.6H_2O$; and schönite, $MgSO_4.K_2SO_4.6H_2O$. The equilibrium conditions are illustrated by the diagram, Fig. 6. The co-ordinate axes [20] are *AOC* and *BOD*; the quadrant *AOB* is used for the binary mixtures $(KCl)_2$ and $MgCl_2$, and the contained curve is indicated with more detail in Fig. 6. The quadrant *AOD* includes binary mixtures of K_2Cl_2 and K_2SO_4; *DOC*, binary mixtures of K_2SO_4 and $MgSO_4$; and the fourth quadrant, *COB*, binary mixtures of $MgCl_2$ and $MgSO_4$. The temp. axis is directed from the plane of the paper towards the reader; the surface areas represent soln. sat. with respect to the salts indicated in the diagram; the lines represent soln. sat. with the two salts indicated in adjoining areas; points below the faces of the solid figure represent unsaturated soln.; the points outside the solid figure represent unstable supersaturated soln.

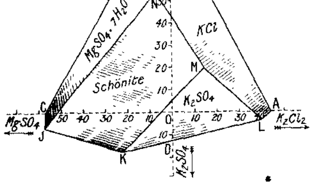

FIG. 6.—Equilibrium Conditions of Mixtures of Magnesium and Potassium Sulphates and Chlorides—J. H. van't Hoff.

The origin of the Stassfurt deposits.—It is generally thought that the Stassfurt beds are of marine origin,[21] and have been formed by the natural evaporation of water during countless years in an immense inland prehistoric sea. This sea must have been periodically replenished by water bringing in more salts, since the Stassfurt deposits contain a larger proportion of calcium salts than obtains normally in sea water, and it is therefore thought that the inland sea must have been fed by fresh-water affluents. As J. Usiglio has shown, gypsum would be first deposited, and this would be converted into anhydrite by the action of sea water

at about 25°, for, although gypsum is formed by the evaporation of a soln. of calcium sulphate, crystals of anhydrite are produced when a soln. of calcium sulphate in conc. brine is evaporated at about 30°. J. Walther supposes that the sea extended from the Ural Mountains to the Scandinavian mountains, and Ireland; and that a torrid climate prevailed which favoured rapid evaporation. The inland sea gradually evaporated, and shrunk, and the last remains completely dried up in Germany. Rivers and streams probably carried the salt from marginal regions towards the central basin in Germany. The order in which the salts are deposited from the evaporation of sea water is very nearly the same as the geological succession observed at Stassfurt.

The work of J. H. van't Hoff shows that the slow evaporation of sea water furnishes successively: (1) a deposit of sodium chloride; (2) sodium chloride mixed with magnesium sulphate; (3) sodium chloride and leonite; (4) sodium chloride, leonite, and potassium chloride; (5) sodium chloride, kieserite, and carnallite; (6) sodium chloride, kieserite, carnallite, and magnesium chloride; and (7) the soln. dries without further change. Consequently, in the formation of the Stassfurt deposits, the brine, enriched with calcium salts, deposited (i) much calcium sulphate and rock salt; the supernatant liquid rich in magnesium salts, and still containing some calcium sulphate, formed (ii) the polyhalite beds. As the conc. of the magnesium salts increased, (iii) kieserite began to separate out. H. Precht and B. Wittzen have shown that the dehydrating action of magnesium chloride prevents the formation of epsomite when a mixture of the sulphate and chloride of magnesium is evaporated on a water bath. After kieserite had been formed, (iv) carnallite was produced.

All the salts found in the Stassfurt deposits have not been formed directly from the conc. of sea water. The layer of mud—saliferous clay—served to some extent to protect the salts from the action of percolating waters, but not entirely, for, in some cases, the salts have been completely leached away and accumulations of gypsum and clay alone remain. This appears to have been the case, for instance, in certain parts of Hannover; in the other cases, only the more soluble magnesium chloride has been leached from the potassium salts. The kainite layers lying above the carnallite layer are thought to have been formed by the action of percolating water on carnallite in the presence of kieserite, because carnallite in the absence of kieserite forms sylvite. The deposits of salts from the inland sea was covered by a layer of clay, and buried to a great depth by bunter shales. Subsequent geological upheavals have tilted the strata in some localities, *e.g.* Fig. 1, and in other places—*e.g.* *in the Eichfeld district between the Harz and the Thuringen forest*—the strata are almost horizontal.

Uses of the Stassfurt salts.—The magnesium compounds in the Stassfurt salts are used for the preparation of magnesium and of its salts. The potash salts are an essential constituent of many fertilizers used in agriculture, etc.;[22] and potassium chloride is the starting-point for the manufacture of the many different kinds of potassium salts used in commerce—carbonate, hydroxide, nitrate, chlorate, chromate, alum, ferrocyanide, cyanide, iodide, bromide, etc. Chlorine and bromine are extracted by electrolysis and other processes from the mother liquids obtained in the purification of the potash salts. Boric acid and borax are prepared from boracite. Cæsium and rubidium are recovered from the crude carnallite and sylvite.

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§ 4. The Extraction of Potassium Salts

> Potash is both wealth and weapon. . . . Our position as sole producer gives us the power of causing grave injury to the agriculture of our enemies by stopping the export of salts so indispensable to them for manurial purposes. . . . If raw materials are refused us we shall revenge ourselves on enemy agriculture with this war cry: At the enemy with a kilo of potash.—VOSSISCHE ZEITUNG (23 November, 1917), and O. N. WITT (1915).

The Stassfurt deposits have enabled the Germans to crush serious competition by underselling the potash derived from other sources. The prices were then raised. The German Potash Syndicate thus acquired an almost exclusive monopoly of the world's market, and compelled the world to pay them tribute. During the Great War supplies were cut off, and the threat of a serious potash famine in the agricultural world rendered it necessary to explore all possible sources of supply. As a result a kind of stock-taking of the world (outside Germany) was made, and some extinct industries were revived.

The chief sources of potash[1] are: (1) The deposits of soluble potash minerals at Stassfurt (Germany), Alsace (France), Galicia (Austria), Catalonia (Spain), Punjab (India), and Atacama (Chili). (2) Sea water, brines, and many lake deposits contain appreciable quantities of potash associated with the sodium salts. (3) The ashes of vegetation—*e.g.* wood ashes, beet-root residues, seaweeds, sunflower stalks, hedge trimmings, etc. (4) The soapy water used for washing the grease from wool.

(5) Products resulting from the decay of organic matter—*e.g.* Indian nitre and South African nitre. The value of saltpetre for the manufacture of gunpowder and in the chemical industries is greatly in excess of its value as a fertilizer; and consequently nitre is not usually regarded as a source of potash supply. (6) Blast furnace and cement-kiln dust. (7) The insoluble potash minerals—*e.g.* felspar, alunite, leucite, etc.

Sea water and brines.—Nearly 2 per cent. of potassium chloride is contained in the 3·5 per cent. of solids in soln. in sea water; hence 10,000 parts of sea water contain 7 parts of potassium chloride. The potassium chloride accumulates as impure carnallite in the mother liquids remaining after the separation of sodium chloride, and it can be recovered by crystallization. The salt-gardens at Geraud en Caraquet,[2] at the mouth of the Rhone, marketed potassium chloride about 80 per cent. purity before further developments were impeded by competition with the Stassfurt deposits. A low-grade potassium chloride, however, can be obtained as a by-product from the bittern of the solar refineries manufacturing common salt from sea water and the brines of saline lakes. The brine from Searles Lake or Searles Marsh, San Bernardino County, California, contains 30·34 per cent. of total solids dried at 110°, or 29·65 per cent. of anhydrous solids containing 2·17 per cent. of its weight of potash K_2O.[3] In the Searles basin, the brine is pumped to storage tanks and distributed to evaporating vacuum pans. The sodium chloride, sulphate, and carbonate deposited at the bottom of the vacuum pans are removed. The liquor is then boiled down to the point where potassium chloride begins to separate. The hot liquor (90°–95°) is then run to the crystallization vats and allowed to cool. The mother liquor is drained from the crop of crystals of the crude potash salts, and returned to the system. A. de Ropp gives the following data:

	$Na_2B_4O_7$	Na_2CO_3	NaCl	Na_2SO_4	KCl	H_2O	Sp. gr.
Raw brine . .	1·50	4·70	16·50	6·90	4·75	60·65	1·290 (30°)
Conc. liquor . .	8·81	10·82	9·67	2·58	14·87	53·25	1·384 (30°)
Mother liquor .	7·82	10·53	9·43	2·08	10·82	59·32	1·362 (34°)
Crude potash salts .	10·91	1·70	10·93	0·44	66·34	9·66	—

The salt-crusted surfaces of the brackish lakes in the South Plains of West Texas are said to contain proportions of potash which can be profitably extracted.

Kelp ash.—The crofters about the rocky shores of West Scotland, Ireland, North-western France, and Japan used to burn the drift-kelp as a fuel, and scatter the ashes over the land as a fertilizer. The great success of kelp ash led to a rapid expansion of the business, so that at the beginning of the nineteenth century kelp harvesting was a flourishing industry. The potash originally employed in the arts and industries was mainly derived from kelp—the ashes of seaweed—and from barilla—the impure alkali obtained from the ashes of plants growing on the sea-shore. The ashes were mixed with varying proportions of sand, which during the incineration or sintering formed some silicates. The mass was lixiviated with water, and then decanted; the filtered liquid was fractionally crystallized by evaporation.[4]

Wood ashes.—The ash of wood, not coal, contains about 30 per cent. of potassium carbonate. Prior to the exploitation of the Stassfurt salts about the middle of the nineteenth century, the chief source of potash was wood ashes, and the process is still used in certain localities where wood-fuel is employed and where much waste wood is available—*e.g.* in some parts of Canada, United States, Russia, Spain, etc. The ash of trees, hedge-cuttings, sawdust, etc., can be made to yield potash.[5] In the Caucasus, the sunflower is grown on waste land for the sake of its seed. The stalks, leaves, etc., are a by-product and are burnt; the ash is used as a source of potash. Nearly 7000 tons per annum of crude potash from this source were exported from Novorossik in Russia. The residues in the manufacture of olive oil and almond shells are also stated by G. l'Abate to be exceptionally rich in potash salts; F. W. F. Day claims that the roots of the water hyacinth (*eichornia crassipes*) have

a high potash content, for they furnish 15 per cent. of ash with about 25 per cent. K_2O; and R. H. Ellis claims that banana skins furnish 1·77 per cent. of ash, which in turn contains 57·16 per cent. of potash. The following data, compiled by W. Savage, represent the percentage weights of the given constituents present in the ashes of normal crops from an acre of ground:

	SiO_2	K_2O	CaO	PO_4	SO_4	Cl	MgO	Na_2O	Fe_2O_3
Grain	14·71	14·39	2·24	35·76	0·12	0·02	7·60	7·05	1·11
Straw	233·08	32·73	27·62	10·56	12·15	3·55	12·14	1·21	5·96
Roots	27·03	142·66	46·24	25·77	46·24	12·24	18·16	17·31	4·35
Tops	2·67	88·82	72·14	28·80	38·81	49·75	9·58	16·76	2·67
Hay	28·23	38·22	44·45	15·12	9·20	4·06	7·09	12·05	0·58

Under ordinary circumstances crops cannot be specially grown for the sake of their potash since the soil would be rapidly depleted of this valuable constituent. In special districts, however, it may be profitable to burn wood in pits sheltered from the wind, and extract the ashes with water.

The ash is mixed with 5 to 10 per cent. of slaked lime and placed in wooden barrels with false bottoms. Hot water is poured over the mixture, and, after standing for some time, the liquid is drawn off from time to time by removing a plug near the bottom of the cask. The liquid with a sp. gr. over 1·15 is evaporated; the low sp. gr. liquor may be used for lixiviating more ash; and the residue in the barrels may be used as manure. The evaporation of the densest liquor to dryness is conducted in cast-iron pots, and the residue is afterwards calcined in a reverberatory furnace to burn away the organic matter—at the same time sulphates may be converted into sulphides. The product is crude *potash*. The crude potash may be mixed with sawdust and re-calcined. It is then digested with twice its weight of hot water, filtered, and cooled. The less soluble impurities—mainly potassium sulphate—crystallize out, and finally the mother liquid is evaporated to dryness and calcined as before; or the soln. may be evaporated until crystals of potassium carbonate are deposited.

The purified product is called *white refined potash*, and also *pearlash*. Some samples of American potash are reported to the following composition:

American potash	K_2CO_3	KOH	K_2SO_4	KCl	Na_2CO_3
Third grade	26·2	26·5	10·4	1·7	2·8
Second grade	34·5	29·6	15·0	7·5	3·0
First grade	26–42	36–49	4–10	1–2	1–3
American pearlash	65–71	—	14–21	3–7	2–4

The vinasse of sugar beet.—Sugar beet contains about 0·5 per cent. of potash, K_2O, largely in combination with organic acids. The potash accumulates in the molasses of the best sugar factories. The molasses are fermented and distilled for alcohol. The residue which remains in the retort—called *vinasse*—may be used as a manure, or it may be mixed with lime and ignited to form what was once called *vinasse cinder*, and used in the manufacture of soft-soap. It is, however, more profitably refined for potash by fractional crystallization.[6] The product has approximately the composition:

K_2CO_3	K_2SO_4	KCl	Na_2CO_3	Insoluble
30 to 35	6 to 8	18 to 22	18 to 20	·15 to 28 per cent.

Wool fat or suint.—The potash found in plants is obtained from the soil; and the potash in the soil is one product of the decomposition of rocks which form the earth's crust. The potash which herbivorous animals—*e.g.* sheep—draw from the land is largely exuded as an oily sweat from the skin, and called, after the French, *suint*. In the first century of our era, Dioscorides called the mixture of wool fat and water οἴσυπος, *œsypus*, a name which it retained up to the middle of the seventeenth century. Œsypus is mentioned several times by Ovid. In spite of its disagreeable smell it appears to have been used by the Roman ladies as one of their choice cosmetics. It is mentioned in N. Culpeper's *Pharmacopœia Londinensis* (London, 1653), but it soon afterwards disappeared from the pharmacopœia

along with other grotesque yet antique remedies—*e.g.* burnt swallows, fox's lungs, crab's eyes, stag's pizzle, boar's tooth, man's skull, etc. In 1882, O. Braun and O. Liebreich patented a preparation which they called *lanoline*. Their process is virtually that described by Dioscorides and by Pliny.[7] The suint accumulates in the wool so that it may form as much as one-third the weight of raw merino wool. The liquid in which wool is first washed contains most of the suint. This liquid can be evaporated to dryness and heated in iron pots or retorts. Potassium carbonate is extracted from the residue by lixiviation with water as indicated above. Dried suint potash contains:

	K_2CO_3	K_2SO_4	KCl	Na_2CO_3	Insoluble
First grade	93·0	0·5	2·0	4·5	0·04
Second grade	87·0	5·1	4·9	2·7	0·03

The annual production of potash from suint in 1913 amounted to between five and ten thousand tons.

Insoluble silicates.—Although the felspathic minerals are slowly decomposed by atm. agencies, the rate of the surface decomposition is too slow to render ground felspar particularly useful as a source of potash for fertilizing soils, although the valleys and flats, which collect the drainage from hills of felspathic rocks, are usually favourable for crops requiring large supplies of potash. The speed of decomposition is much facilitated if the felspar be ground excessively fine,[8] and in 1910, F. R. Carpenter patented the pre-calcination and sudden quenching of the mineral in order to make the contained potash dissolve more quickly in the soil water. Ground alunite, or better, alunite calcined and ground, is used directly as a potash fertilizer in some parts of the United States; similar remarks apply to the use of ground leucite in Italy; and the use of ground phonolite in Iceland.

Numerous processes have been proposed for extracting potash from felspar, leucite, alunite, and other minerals rich in this substance, but the cost is so great that very few proposals yet made offer promise of successful competition with the Stassfurt deposits. This is even the case with alunite, where mere calcination to 1000° drives off water and sulphuric acid, leaving water-soluble potassium sulphate, and alumina. Humphry Davy in his paper: *On Some Chemical Agencies of Electricity* (1807), indicated in Cap. III, found that when water was electrolyzed in cavities contained in celestine, fluorspar, zeolite, lepidolite, basalt, vitreous lava, agate, or glass, the bases separated from the acid and accumulated about the cathode. It is therefore probable that if water with finely divided potash minerals in suspension were electrolyzed, the alkali would be separated in a convenient simple way.

In their study: *The production of available potash from the natural silicates*, A. S. Cushman and G. W. Coggleshall reviewed the methods which have been proposed for extracting water-soluble potash salts from natural silicates. These may be arranged in three groups. There is a dreadful monotony in various patents, for in spite of their great number, very rarely does a novel principle appear which offers any promise of success.

(1) *Wet processes.*—In 1894, H. S. Blackmore[9] tried subjecting a mixture of lime, calcium chloride, and felspar to the action of steam in an autoclave; and ten years later, he further proposed to treat a slurry of the powdered mineral with carbon dioxide under a press. of 500 lbs. per sq. in. in order to produce potassium carbonate. Neither proposal has been successful. In 1865, H. le Chatelier proposed to release the potash by mixing the powdered mineral intimately with caustic lime and soda ash and arranging the mass in heaps, kept moist with water for about a month. G. Levi (1904), A. Piva (1905), A. J. Swayze (1907), and W. T. Gibbs (1909)[10] proposed digesting the powdered mineral with soln. of the alkalies or alkaline earths under press. W. T. Gibbs (1904) also proposed to treat the mineral first with hydrofluosilicic acid and then with sulphuric acid in order to prepare potassium sulphate; and A. S. Cushman proposed mixing a slurry of the mineral with hydrofluoric acid, and electrolyzing the mixture in wooden vats provided with diaphragms. Alumina and potash collected in the cathode compartment. W. T. Gibbs[11] fused a mixture of felspar, lime, or alkali carbonate in an electric furnace, and recovered the alkali from the slag; W. T. Gibbs used phosphate rock in place of lime.

S. Peacock heated a mixture of powder felspar and coal in a reducing atm., and treated the product with superheated steam in an autoclave in order to recover the water-soluble potash. B. F. Halvorsen heats to 650° a mixture of ground felspar, cyanamide, and alkali salts with superheated steam. Ammonia and soluble potash are formed. H. W. Charlton digested greensand with lime and water in an autoclave.

(2) *Dry volatilization process.*—Potassium salts are found in the fumes emitted by blast furnaces and cement kilns. Various proposals have been made in which the powdered mineral mixed with suitable fluxes—and in some cases with carbon—is heated in shafts in rotary kilns at a temp.—say 900°—in order to volatilize the potash salts. A. J. Swayze (1905)[12] used gypsum and carbon and collected the volatilized sulphate; A. C. Spencer and E. C. Eckel (1909) clinkered a mixture of greensand with calcareous and siliceous fluxes—a kind of Portland cement was obtained as a by-product. Similarly, B. Herstein fritted a mixture of felspar, calcium chloride, and chalk. In E. W. Jungner's method a mixture of felspar with three times its weight of calcium carbonate was calcined between 1400° and 1450° in a rotary kiln. H. E. Brown heated a mixture of coal or coke, powdered felspar and limestone in a blast furnace—the fused mass was run into a cooling apparatus and ground for cement; the potash largely passed off with the furnace gases and was collected as dust. J. N. Carothers fused phosphate rock in an electric furnace, and collected the potash fume evolved.

(3) *Dry processes.*—In 1856, C. Bickell[13] heated a mixture of felspar, lime, and a natural phosphate or guano to a bright redness; and the *Societa Romana Solfati* roasted a mixture of leucite with alkali—carbonate, hydroxide, or nitrate—lime, and carbon at a red heat. When steam was passed through the mass, sodium aluminate and potassium carbonate were obtained. F. O. Ward and F. Wynants fritted felspar with fluorspar and lime. The soluble potassium silicate obtained by lixiviation with water was decomposed with carbon dioxide. A. R. Linblad[14] fused a mixture of felspar, coal, and iron ore in an electric furnace, the soluble potash was obtained by lixiviation of the product with water; C. W. Drury fused a mixture of felspar, lime, and iron oxide (hæmatite), and extracted the potash by lixiviation with weak acids. J. G. A. Rhodin (1900)[15] fritted together a mixture of felspar, lime, and salt; R. H. McKee (1907) fritted micaceous minerals with lime, carbon, and salt; A. S. Cushman (1911) fritted a mixture of felspar and lime and a salt of a mineral acid capable of decomposing the felspar. W. E. Wadman fritted lepidolite with potassium sulphate and obtained lithium sulphate when the mass was leached with sulphuric acid. In 1911, F. Thompson[16] heated a mixture of felspar, sodium acid sulphate (nitre cake), and sodium chloride. The potassium sulphate formed was leached out with water. In the same year, E. Hart fritted the felspar with barium sulphate and lime, potash alum passed into soln., and there remained a mixture of silica and barium sulphate said to be useful as a white pigment.[17]

Cement kiln and blast furnace flue-dust.—In 1904, E. Cramer[18] pointed out that the clouds of dust deposited in the drying chamber of Portland cement works utilizing the waste gases for the drying, contain notable amounts—56·35 per cent. —of soluble alkalies. The soluble portion contained 61·1 per cent. of potassium sulphate, and 38·9 per cent. of potassium carbonate. The proportion of silica in the insoluble portion was found to be too high for it to have come from the cement. In the same year, C. Richardson showed that with the prices then ruling, the recovery of the dust promised not only to be a profitable operation, but also offered hygienic advantages for the workers. According to K. M. Chance, also, the dust in the gas-cleaning plant of blast furnaces manufacturing pig-iron contains enough potash for profitable extraction, and if the ore be salted, the yield of potassium chloride is increased from 30 to 200 lbs. per million cub. ft. of gas.

Two systems are in vogue for the recovery of alkali from cement or blast furnace dust—electrical precipitation by Cottrell's process, and the water-spray system. In the latter process, the gases leave the cement calcining kiln at 380°, and pass through a dust-settling chamber where the temp. has fallen to about 230°; the gases then pass into a spraying chamber, and the water thence runs through condenser tubes where much of the water is evaporated. The liquid is filtered to separate insoluble mud, etc., and evaporated for crystallization. The accumulation in the dust chamber is likewise leached with water, filtered, and evaporated. A great deal of potash fume was found to escape wetting by the water spray and was lost unless elaborate gas-scrubbers or coke-towers were employed for the fumes leaving the spraying chamber. The troubles connected with the collection of the dust have been largely overcome by passing the gases through insulated tubes where the fine dust is electrified and condensed. The salting of the ores used in blast furnaces is said

to facilitate the volatilization of the potash. According to E. C. Rossiter, and C. S. Dingley, about 80 per cent. of the total potash in the furnace charge can be recovered from the North Lincolnshire ores; similarly with blast furnaces using hæmatite ores; and about 33 per cent. of the potash in furnaces using Cleveland ores. It is estimated that the blast furnaces of England and Wales can furnish 63,292 tons of potassium chloride per annum.

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§ 5. The Extraction of Lithium, Rubidium, and Cæsium Salts

The five alkalies frequently occur together so that in almost all cases of extraction, it is necessary to separate the alkalies from one another. Lithium can be separated from the other members of the alkali family by taking advantage of the ready *solubility of its chloride in amyl alcohol (F. A. Gooch)*,[1] *in absolute ether and alcohol* (C. F. Rammelsberg), in primary butyl alcohol (L. W. Winkler), or in pyridine (L. Kahlenberg, F. C. Krauskoff); the sparing solubility of the phosphate in water (J. J. Berzelius, and W. Mayer) or in ammoniacal soln. of ethyl alcohol (R. Benedikt); the sparing solubility of the carbonate (H. Müller), or fluoride (A. Carnot); or the ready solubility of the fluosilicate (C. Reichard). Potassium, rubidium, and cæsium can be separated from sodium and lithium by taking advantage of the sparing solubility of the chloroplatinates of potassium, rubidium, and cæsium. If thallium be present, it will be precipitated as a sparingly soluble thallous chloroplatinate,

Tl_2PtCl_6, along with the rubidium and cæsium; but thallous salts are precipitated by ammonium sulphide; by hydrochloric acid; and particularly by potassium iodide. Potassium, rubidium, and cæsium can also be separated from the other two alkali metals by taking advantage of the sparing solubility of the potassium, rubidium, and cæsium alums. Potassium can be separated from rubidium and cæsium by taking advantage of the greater solubility of potassium chloroplatinate, or of potash alum, or of potassium silicomolybdate (F. Parmentier) in water. Cæsium and rubidium can be separated from one another by taking advantage of the difference in the solubility of the chloroplatinates, of the alums, or of the oxalates (J. Formánek), by the formation of a more stable and less soluble rubidium tartrate (R. Bunsen); by the greater solubility of cæsium carbonate in absolute alcohol (R. Bunsen); by the very sparing solubility of the double chloride and iodide of cæsium, $CsCl_2I$ (H. L. Wells); [2] cæsium lead iodide, $CsPbI_6$ (H. L. Wells); cæsium antimony chloride, $Cs_3Sb_2Cl_9$ (F. Godeffroy); cæsium stannic chloride, Cs_2SnCl_6 (S. P. Sharples).

Lithium.—In order to extract lithium from the silicate minerals—petalite, lepidolite, spodumene, amblygonite, etc.—J. J. Berzelius [3] fused the finely powdered mineral with twice its weight of calcium or barium carbonate. L. Troost fused a mixture of finely powdered lepidolite with an equal weight of barium carbonate, half its weight of barium sulphate, and one-third its weight of potassium sulphate. In the latter case, two layers were formed; lithium and potassium sulphates accumulated in the upper layer from which they were extracted by simple lixiviation. The sulphates are converted to chlorides by treatment with barium chloride. The filtered liquid is evaporated to dryness, and the chlorides extracted with a mixture of absolute alcohol, or pyridine. The lithium chloride dissolves, the other alkali chlorides remain as an almost insoluble residue.

F. Filsinger [4] decomposed finely ground lepidolite by mixing it with conc. sulphuric acid and igniting the mixture up to, say, 340°. The mass is extracted with water. The silica may be filtered off, and the aluminium sulphate converted into potash alum by treatment with potassium sulphate; on standing, most of the alum separates as crystals, the remainder is removed by making the soln. alkaline with lime water, adding calcium carbonate and freshly precipitated aluminium hydroxide, and boiling briskly. Practically all the alumina separates as basic alum or alunite. The filtrate is conc. by evaporation, and the lime precipitated by treatment with oxalic acid; the iron and manganese are precipitated by potassium hypochlorite or ammonium sulphide. The crude soln. of lithium sulphate so obtained is treated with potassium or ammonium carbonate to precipitate lithium carbonate. The mineral triphylite, $Li(Fe, Mn)PO_4$, is also a source of lithium. It is decomposed by acids. R. F. Weinland and L. Storz treated the finely powdered mineral with aqua regia, and evaporated the mass to dryness with frequent additions of hydrochloric acid so as to remove the nitric acid. The remaining mass was extracted with hot water, and the liquid treated with an excess of milk of lime; the filtrate was treated with a soln. of ammonium carbonate in ammonia, filtered, evaporated, and heated to drive off the ammonium salts. The lithium chloride was extracted from the dry residue with a mixture of absolute alcohol and dry ether. The extract was evaporated to dryness, and re-extracted with the same solvent until the lithium chloride obtained coloured the non-luminous gas-flame dark red. H. Müller [5] treated the same mineral with hydrochloric acid, oxidized the iron with nitric acid, precipitated the phosphoric acid by the addition of a ferric salt, and evaporated the filtrate to dryness. The manganese and lithium chlorides were dissolved by extracting the dried mass with hot water, and the manganese precipitated by the addition of barium sulphide. The excess of barium was removed by sulphuric acid. Lithium oxalate was obtained by evaporation with oxalic acid, and the oxalate was converted into carbonate by ignition.

The purification of lithium salts.—The lithium salts prepared by the above described processes contain salts of the alkalies and alkaline earths. These

impurities are very difficult to eliminate. In 1856, J. W. Mallet[6] purified the chloride by dissolving it in a mixture of alcohol and ether, but J. S. Stas has shown that repeated treatment by this solvent is not sufficient to remove the alkali chlorides; K. Diehl repeatedly precipitated lithium by ammonium carbonate, some thirty precipitations were required to free it from sodium. L. Troost repeatedly dissolved lithium carbonate in cold water sat. with carbon dioxide, and reprecipitated the lithium carbonate by boiling the soln.; but W. Dittmar failed to obtain a pure salt by this means. J. S. Stas tried to purify lithium salts by a combination of Diehl's and Troost's processes, but he failed to prepare a sample which did not show the sodium line upon very careful spectroscopic examination. He volatilized one-third or one-half the carbonate in the oxyhydrogen flame and obtained a residue of oxide free from sodium, but he failed to prepare lithium chloride from this oxide free from sodium, and he remarked: *C'est l'impossibilité de préparer du chlorure de lithium ne donnant pas la raie sodique.* However, T. W. Richards and H. H. Willard did prepare lithium salts of a high degree of purity in the following manner:

A boiling soln. of ammonium fluoride was poured into a boiling soln. of lithium salt, slowly and with constant stirring. An excess of either salt was avoided. The coarsely crystalline lithium fluoride so obtained was washed several times with water. A repetition of this treatment sufficed to give lithium fluoride spectroscopically free from sodium. To eliminate calcium and magnesium, the lithium fluoride was converted into the corresponding nitrate or perchlorate by heating it in a platinum retort with the corresponding acid. Three or four times the theoretical quantity of nitric acid was required for the conversion. The salts were recrystallized several times with centrifugal drainage, and no calcium, or magnesium, or sulphate could be then detected by the ordinary chemical tests. The nitrate can be converted into carbonate by pouring a soln. of the lithium salt into a hot conc. soln. of ammonium carbonate, and washing the coarsely crystalline precipitate several times in hot water.

Lithium, rubidium, and cæsium.—F. C. Robinson and C. C. Hutchins[7] extracted all three alkalies—lithium, rubidium, and cæsium—by decomposing the mineral with fluorspar in the following manner:

An intimate mixture of equal parts of finely ground lepidolite and fluorspar—say, 100 grms. lepidolite—is stirred with sulphuric acid in a lead or platinum dish so as to form a thin slip. When the fumes of silicon fluoride, etc., have nearly ceased to be evolved, heat the mixture on a sand bath or hot plate between 200° and 300° until the residue is dry and hard. Extract the mass with hot water until a few drops of the washings give no precipitate with aq. ammonia. Evaporate the soln. down to about 100 c.c., and filter the hot liquid so as to remove calcium sulphate. The conc. soln. is sat. with ammonium alum and allowed to stand for some time. The mixed crystals of potassium, rubidium, and cæsium alums and of lithium salt are dissolved in 100 c.c. of distilled water and recrystallized. The recrystallization is repeated until the crystals show no spectroscopic reaction for potassium or lithium. The yield naturally depends on the variety of lepidolite employed. 100 grms of an average sample gives about 10 grms. of crude crystals; and about 3 grms. of the purified cæsium and rubidium alums. For the purification of cæsium and rubidium salts, see the chlorides. The mother-liquors are treated with an excess of barium carbonate, boiled, and filtered. The filtrate is acidified with hydrochloric acid, and evaporated to dryness. The residue is extracted with absolute alcohol in which lithium chloride is soluble, and the other alkali chlorides are sparingly soluble.

Rubidium and cæsium.—One of the most important sources of rubidium is the mother-liquor remaining after the extraction of potassium chloride from carnallite. The mother-liquid contains rubidium carnallite, $RbCl.MgCl_2.6H_2O$, and cæsium carnallite, $CsCl.MgCl_2.6H_2O$. Aluminium sulphate is added to the soln. and the alums of cæsium and rubidium are separated by fractional crystallization. These two alkalies are also obtained from the mother liquids remaining, after the extraction of salt from sea water.[8] R. Bunsen, it will be remembered, obtained these two alkalies from the mother-liquid furnished by the evaporation of nearly fifty thousand kilograms of the mineral waters of Dürkheim; and R. Böttger obtained them from the waters of Nauheim. The mother-liquid of the nitre refineries also furnishes these alkalies.[9]

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§ 6. The Preparation of the Alkali Metals

The key to a knowledge of Nature's methods is her analogies.—R. OTTOLENGUI.

When any apparently exceptional or new substance is encountered, the chemist is guided in his treatment of it by analogies which it seems to present with previously known substances.—W. S. JEVONS.

Discoveries in science are very often made by following up hints received from analogies. The history of fluorine has taught the value of analogy as the source of prophetic conjecture, and the isolation of the metals potassium and sodium is another good illustration.[1] At the beginning of the nineteenth century, the so-called alkalies and alkaline earths—magnesia, lime, and potash—were considered to be elementary substances. A. L. Lavoisier proved that some things resembling the earths—*e.g.* tin oxide, iron rust, mercuric oxide—could be resolved into two substances, oxygen and a metal. By analogy, Lavoisier inferred, in 1793, that the indifference of the earths for oxygen is due to their being already oxidized, and he ventured to predict that they are not the simple substances, for he conjectured that it would be possible to resolve them into the corresponding metals and oxygen. It was reserved for H. Davy to realize this prognostication, after it had been shown that the electric current could resolve water and certain salts into their elements. H. Davy tried if the electric current would work in an analogous manner on caustic soda and caustic potash. As a result, Davy isolated the metal potassium on October 6, 1807, and sodium a few days afterwards. It is related that Davy was so elated with the success of his experiment that he could not contain his joy, but bounded about the room in an ecstasy of delight.

H. Davy [2] exposed a piece of solid potassium hydroxide to the atm. for a few seconds so that a conducting film of moisture formed on the surface. The piece of

potash was then placed on an insulated disc of platinum connected with the negative pole of a battery, and a platinum wire connected with the positive pole was brought in contact with the upper surface of the potash. Davy added:

Under these circumstances a vivid action was observed to take place. The potash began to fuse at both its points of electrification. There was a violent effervescence at the upper surface; at the lower, or negative surface, there was no liberation of elastic fluid; but small globules having a high metallic lustre, and being precisely similar in visible character to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surface. The globules numerous experiments soon showed to be the substance I was in search of, and a peculiar inflammable principle, the basis of potash.

This discovery was soon followed by the isolation of barium, strontium, and calcium. By analogy, it was further inferred that all amorphous powders—alumina, magnesia, etc.—possessing similar properties, were metallic oxides. As a result, when a new earth is now discovered, chemists believe, by faith, that it is the oxide of a metal even in cases where the supposed metal has never been isolated.

N. M. Hopkins[3] has given the following simple modification of Davy's experiment: A small cavity is made in a block of sodium hydroxide, and the block moistened with water. The block is placed on a piece of sheet platinum or nickel. Mercury is poured into the cavity, and a platinum or nickel wire, dipping in the mercury, is connected with the negative lead of a direct current of electricity; the plate of platinum or nickel is connected with the positive lead, as indicated in Fig. 7. During the electrolysis the sodium hydroxide is moistened from time to time. After about an hour, the mercury becomes immobile owing to the amalgamation of sodium with the mercury. The two metals can be separated by distilling off the mercury; sodium remains behind.

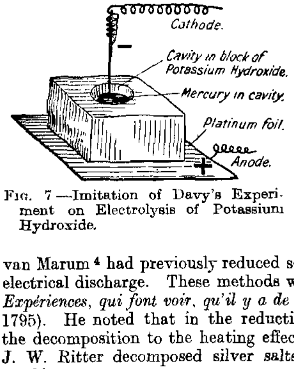

Fig. 7.—Imitation of Davy's Experiment on Electrolysis of Potassium Hydroxide.

Humphry Davy's process for the isolation of the alkali metals by the aid of the electric current is now regarded as the foundation of dry electrometallurgy, and justly so in spite of the fact that M. van Marum[4] had previously reduced several compounds by subjecting them to the electrical discharge. These methods were described in M. van Marum's pamphlet: *Expériences, qui font voir, qu'il y a de la calorique dans la fluid électrique* (Haarlem, 1795). He noted that in the reduction oxygen gas is evolved, and he credited the decomposition to the heating effect of the electric current. A few years later, J. W. Ritter decomposed silver salts by the discharge from a small electrical machine.

The alkali metals are strongly electro-positive, and their affinity for oxygen is great. The extraction of such metals from their compounds—oxides or halides—requires the use of powerful reducing agents often at a high temp. Such operations are usually costly and difficult. The electrolysis of aq. soln. is not practicable because the deposited metal immediately reacts with the solvent, but in some cases—*e.g.* lithium—the metal can be deposited by the electrolysis of soln. of the salts in solvents which do not decompose the deposited metal. The most direct process of preparing the alkali metals is to electrolyze the anhydrous and fused hydroxide or salts. In spite of the losses involved in generating electrical energy, electrolysis is often the cheapest way of extracting the light metals. Those compounds which melt at a comparatively low temp. are preferred, otherwise the cost of maintaining the temp. and the corrosive action of the fused salt on the containing vessel and the electrodes become a serious factor in industrial work. With sodium, the fused hydroxide is preferred as electrolyte; it melts at about 318°, whereas the chloride

melts at 801°. Sodium boils at 877°, and at the m.p. of the chloride the vap. press. is high. Sodium is the only metal in the alkali family which is produced commercially on a large scale; potassium is obtained commercially by the electrolysis of fused potash, but, in view of the higher cost of potassium salts, and the fact that metallic sodium can be used in place of potassium, relatively small quantities of potassium are made; lithium, rubidium, and cæsium partake more of the nature of chemical curiosities, and are produced on a small scale.

The general methods for the production of the alkali metals are: (1) *Electrolytic processes* involving the electrolysis of (*a*) the fused hydroxide, or (*b*) a fused salt—chloride, nitrate, cyanide, etc. (2) *Chemical processes* involving the reduction of hydroxide, or carbonate, or other salt with carbon, metal carbide, iron, calcium, magnesium, aluminium, etc. W. Spring [5] claims to have reduced a little potassium chloride by passing hydrogen over the salt at a red heat.

Electrolysis of the fused alkali hydroxide.—At the time of Davy's discovery the dynamo had not been invented, and the electric current derived from batteries was far too costly for the production of sodium on a manufacturing scale. In modern works, where cheap electrical energy is available, modifications of Davy's original process—electrolysis of fused sodium hydroxide—are used for preparing sodium industrially—*e.g.* H. Y. Castner's electrolytic process (1890).[6] Potassium can also be made by H. Y. Castner's process.

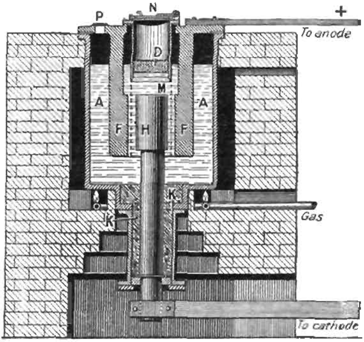

FIG. 8.—Castner's Electrolytic Process for Sodium.

H. Y. Castner's electrolytic process for sodium.—The sodium hydroxide, contained in an iron pot set in brickwork, is melted by means of a ring of gas jets placed underneath; and kept about 20° above the m.p. (318°) of sodium hydroxide. The cathode, *H*, of nickel or iron rises through the bottom of the iron pot, *A*, Fig. 8, and is maintained in position by a cake, *K*, of solid sodium hydroxide in the lower part of the pot. The anodes, *F*, several in number, are suspended around the cathodes from above. A cylindrical vessel, *ND*, floats in the fused alkali above the cathode, and the sodium and hydrogen liberated at the cathode collect under this cylinder. The hydrogen escapes through the cover, and the atm. of hydrogen in the cylinder protects the sodium from oxidation. A cage of nickel wire gauze, *M*, separates the anode, *F*, from the cathode, *H*. From time to time the sodium, *D*, is skimmed off by means of a perforated ladle, which retains the liquid metal, but allows the molten hydroxide to flow back. The oxygen liberated at the anode escapes *viâ* the vent *P*.

Hydrogen is a by-product in Castner's process, and if there be no commercial demand for this gas, its production represents so much wasted energy. The *mechanism of the electrolysis* has been investigated by G. Janeczek and by M. le Blanc and J. Brode.[7] If *commercial sodium hydroxide* is used, the moisture is first electrolyzed giving hydrogen at the cathode, oxygen at the anode; as the electrolysis proceeds, the production of hydrogen becomes more and more difficult, until, at a certain decomposition voltage, sodium appears. If the sodium hydroxide has been previously dehydrated, no hydrogen is evolved before the sodium appears. The hydroxide is electrolyzed $NaOH \rightarrow Na^{\cdot} + OH'$, the sodium appears at the cathode, and, at the anode, the hydroxyl is resolved into water and oxygen. The hydrogen which appears at the cathode is the product of a secondary chemical reaction,

between the sodium at the cathode and the water formed at the anode: $2Na + 2H_2O \rightarrow 2NaOH + H_2$. It is therefore possible to have both hydrogen and oxygen liberated at the anode, and explosions may then result. Sodium and potassium are soluble in their respective anhydrous and molten hydroxides [8]—sodium more so than potassium. The solubility decreases rapidly with temp.—*being* 25·3 *grms. of sodium per* 100 *grms. of hydroxide at* 480°, *and* 6·9 *grms. at* 800°. The secondary reaction between sodium and the water formed at the anode is greater at higher temp. because the rate of diffusion of the metal in the electrolyte is greater under these conditions. The sodium which diffuses to the anode may also react with the oxygen there being evolved, forming sodium peroxide: $2Na + O_2 \rightarrow Na_2O_2$; and the latter may react with more sodium, forming the monoxide: $Na_2O_2 + 2Na \rightarrow 2Na_2O$. These secondary reactions reduce the yield of sodium, and M. le Blanc and J. Brode estimate that the Castner process cannot give higher than a 50 per cent. current-efficiency; they also show that if water could be kept away from the cathode—by, say, a current of dry air [9]—and sodium from the anode—by, say, a non-corrodible cathode diaphragm—the yield might be augmented.

The heat of formation of sodium hydroxide, NaOH, is 102 Cals., and since one joule is eq. to 0·00024 Cal., 102 Cals. are eq. to 425,000 joules; and the minimum *voltage required for the electrolysis of fused sodium hydroxide is* 425,000÷96.540, or 4·4 volts. Thomson's rule gives the decomposition voltage of molten sodium hydroxide, 3·1 volts. O. Sackur,[10] and M. le Blanc and J. Brode found the decomposition voltage of the water present in moist sodium hydroxide to be 1·3 volts at 330°; and for sodium formation, 2·2 volts at 330°. If the average voltage of the current running Castner's cell is 4·5 volts, and there is a current-efficiency of 48 per cent., there is an energy-efficiency of 22 per cent.

G. von Hevesy *obtained greater yields of potassium* by the electrolysis of its hydroxide than of sodium with its hydroxide at the same temp. For example, between 320° and 340°, a 27 per cent. yield of sodium, and a 55 per cent. yield of potassium, were obtained. This was traced to the increased rate of diffusion of sodium from cathode to anode where the metal is lost by secondary reactions; and this the more, the higher the temp. F. C. Wickel and W. Löbel obtained potassium *from its hydroxide and metallic sodium*, by melting the two together in *the absence of air; sodium oxide is formed and potassium distils from the mixture*; hydrogen gas also escapes.

There are other processes analogous to Castner's which involve no new principles and which are used to a limited extent; for instance, with H. Becker's process [11] the form of the cell is modified; and the contact electrode process of the Chem. Fabr. Griesheim-Elektron, where the cathode does not dip into the electrolyte but is merely in contact therewith.

The electrolysis of fused alkali salts.—Many attempts have been made to prepare sodium directly by the electrolysis of the fused chloride, since that salt is by far the most abundant and the cheapest source of the metal. The high fusion temp.; the strongly corrosive action of the molten chloride; and the difficulty of separating the anodic and cathodic products, are the main difficulties which have been encountered in the production of sodium by the electrolysis of fused sodium chloride. Attention has been previously directed to C. E. Acker's process for the preparation of sodium, or rather a sodium-lead alloy, by the electrolysis of fused sodium chloride whereby sodium is produced at one electrode, and chlorine at the other; but the process does not appear to have been commercially successful. In E. A. Ashcroft's abandoned process the fused chloride is electrolyzed in a double cell with a carbon anode, and a molten lead cathode. The molten lead-sodium alloy was transported to a second chamber, where it was made the anode in a bath of molten sodium hydroxide whereby sodium was deposited at the cathode. A. Matthiessen [12] electrolyzed a mixture of sodium chloride with half its weight of calcium chloride; the addition of the chloride of the alkaline earth, said L. Grabau, hinders the formation of a subchloride. J. Stoerck recommended the addition of

20–25 per cent of the alkali fluoride in order to make the electrolyte more fusible. R. Bunsen's failure to obtain rubidium by the electrolysis of the chloride is thought to be due to the formation of the hydride, and not the subchloride as he supposed. E. Linnemann prepared potassium by the electrolysis of fused potassium cyanide; and C. Setterberg prepared cæsium by the electrolysis of a fused mixture of cæsium and barium cyanides. The barium cyanide is added to make the mixture more fusible. In J. D. Darling's process, sodium nitrate was electrolyzed in cast-iron pots, the gases evolved were passed into water so as to form nitric acid as a by-product.

In order to obtain metallic lithium, A. Guntz electrolyzed a mixture of equal parts of lithium and potassium chlorides; and O. Ruff and O. Johannsen obtained better results with a mixture of lithium bromide with 10 to 15 per cent. of the chloride. The electrolysis is conducted in a graphite retort with a thick iron wire as cathode, and a current of 100 amps. at 10 volts gave an 80 per cent. yield.

In R. Bunsen's apparatus, an iron wire and graphite rod dip into the fused chloride without the aid of the clay pipe. In a few seconds, says Bunsen, a small silver-white regulus is formed under the fused chloride round the iron wire, and adhering to it, which, after 2 or 3 minutes, attains the size of a small pea. To obtain the metal, the wire pole and regulus are lifted out of the fused mass by a small, flat, spoon-shaped, iron spatula. The wire can then be withdrawn from the still molten metal, which is protected from ignition by the lithium chloride with which it is coated. The metal, after cooling under rock oil, may now be easily taken off the spatula with a pen-knife. As this operation can be repeated every three minutes, an ounce of lithium chloride can be reduced in a very short time. In F. Hiller's modification,[13] lithium chloride, mixed with ammonium chloride, is heated to its m.p. in a porcelain crucible, Fig. 9. A piece of iron wire, passing through the bore of a "clay" tobacco pipe inverted in the molten chloride, serves as cathode; and a rod of retort carbon serves as anode. For the sake of clearness, the drawing, Fig. 9, has been made as if the parts of the apparatus were transparent. If desired a stream of dry hydrogen gas can be passed into the tobacco pipe so that the liquid about the cathode is not exposed to oxygen. A current from a battery giving 7 to 8 volts serves for the electrolysis of the molten chloride. The reduced lithium rises to the surface of the liquid in the compartment where it is protected from oxidation. Before using the apparatus it is advisable to cover the crucible and pipe with a layer of powdered graphite made into a slip with a dil. soln. of lithium chloride. The coating is dried and baked at a red heat. This prevents the formation of lithium silicide by the action of the fused chloride on the clay. After an hour's electrolysis, the apparatus can be cooled, and the regulus of lithium removed by breaking the pipe.

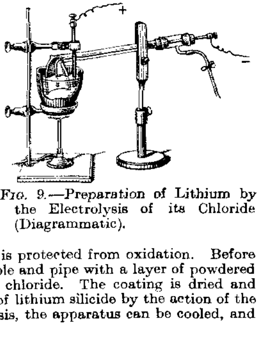

Fig. 9.—Preparation of Lithium by the Electrolysis of its Chloride (Diagrammatic).

Lithium cannot be obtained by the electrolysis of aq. soln. of its salts, but L. Kahlenberg obtained it by the electrolysis of soln. of the chloride [14] in pyridine, acetone, or in various alcohols. Silvery white lithium was obtained from a conc. soln. of lithium chloride in pyridine at the room temp. using a graphite plate as anode, and an iron plate as cathode with 0·2 to 0·3 amp. per 100 sq. cm. of cathode surface, and a potential difference of 14 volts.

Reduction of alkali salts by carbon or the carbides.—In 1808, F. R. Curaudau used charcoal as reducing agent. The reaction is endothermic: $K_2CO_3+2C=3CO+2K-189$ Cals., but at the high temp. of the retort, the thermal value of the process will be very different from this—part of the carbonate, for instance, will be dissociated. It was found important to get an intimate mixture of the alkali and the carbon. This was obtained by heating acid potassium tartrate in a covered crucible. Others have proposed mixing the carbonate or hydroxide with tar, glucose, or other organic compounds.[15] Lithium cannot be prepared by the reduction of the hydroxide or carbonate with carbon as is possible with the other

alkali metals. In F. R. Curaudau's process, the mixture was placed in a wrought-iron "mercury bottle," the exit condensing tube dipped in rock oil. Many improvements in Curaudau's process were introduced by H. Brunner, F. Wöhler, and F. Donny and J. Mareska.[16] In the preparation of the element by the action of carbon on potassium carbonate at a high temp.: $K_2CO_3+2C=2K+3CO$, if the vapour of the potassium be not rapidly cooled, a black explosive compound with the carbon monoxide is said to be formed—**potassium carbonyl,** possibly $K_2(CO)_2$, that is, K—CO—CO—K. Until cheap electric energy was available, H. St. C. Deville's modification of this process was employed. He obtained sodium by strongly heating an intimate mixture of sodium carbonate, coal, and chalk in an iron retort, and condensing the volatilized metal. H. St. C. Deville required considerable quantities of sodium for use in his process for aluminium; and his works at Salindres (France) were the means of reducing the cost of a kilogram of sodium from 2000 francs in 1855 to 10 francs in 1859. Other reducing agents were proposed—for example, H. Y. Castner (1888)[17] used iron carbide—FeC_n. Calcium carbide, CaC_2, has also been used for the same purpose: $6KOH+2CaC_2=6K+2CaO+4CO+3H_2$. The Chem. Fabr. Griesheim-Elektron also patented a process for reducing sodium or potassium fluoride, or fluosilicate, with or without cryolite, by means of calcium carbide.

Reduction of alkali salts by the metals.—Soon after Davy's discovery of the alkali metals, J. L. Gay Lussac and L. J. Thénard (1808)[18] prepared potassium by heating metallic *iron* with potassium carbonate or hydroxide at a white heat: $4KOH+3Fe=Fe_3O_4+2H_2+4K$. The vapour of the liberated potassium was condensed in a copper receiver containing rock oil to prevent the oxidation of the metal. In 1872, C. E. Dolbear proposed to reduce the sulphide with iron filings. Lithium cannot be prepared by reduction with iron as in the case of potassium or sodium. Sodium chloride mixed with powdered *lead* heated red hot in a closed retort gives metallic sodium: $2NaCl+Pb=PbCl_2+2Na$. By heating the alkali chlorides with metallic *calcium*[19] in an exhausted hard glass tube, potassium, cæsium, and rubidium have been prepared. The reaction commences between 400° and 500°, and the heat developed volatilizes the alkali metal which can then be driven into the cooler part of the tube and sealed off. Lithium could not be so obtained because *it furnishes an alloy containing 3 or 4 per cent. of calcium, and from which the latter* metal cannot be readily separated. All the chlorides of the alkali metals are *incompletely* reduced to metals when heated with *magnesium*. The hydroxides or carbonates of the alkali metals—excepting cæsium—are reduced by heating a mixture *of one mol. of the carbonate with three gram-atoms of magnesium. The reduction* is effected in an iron tube previously deoxidized by heating it with a stream of *hydrogen passing along the interior. The reduction is less violent, the higher the* at. wt. of the element. The reaction with lithium proceeds with explosive violence, *and the metal is volatilized; with potassium and rubidium, the reaction proceeds* quickly without any marked volatilization of the metal, although with potassium there is a risk of forming the explosive carbonyl which is eliminated by using the hydroxide. To lessen the violence of the reaction, C. Winkler recommended adding about 40 per cent. of magnesia. With *aluminium* metal in place of magnesium, some alkali aluminate is formed, and the yield is considerably reduced. N. N. Beketoff[20] prepared potassium, rubidium, and cæsium metals in this manner. The Chem. Fabr. Griesheim-Elektron patented a method in which a mixture of aluminium with potassium fluoride or fluosilicate was heated in an iron retort.

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§ 7. The Properties of the Alkali Metals

The properties of the alkali metals and of their salts are roughly functions of the at. wt. of the metals. There is generally a break in the curve about potassium so that lithium and sodium form one series, and potassium, rubidium, and cæsium another. The properties of the series, K, Rb, Cs generally change more regularly than the series Li, Na, K, although some irregularities do occur—*e.g.* the m.p. of the nitrates.

The alkali metals are all silvery white; these metals frequently have a yellow

tinge particularly when reduced from their chlorides by calcium. The colour is due to the presence of impurities, in this case nitrogen, not oxgyen, derived from the air.[1] A. W. Hull[2] found that the X-ray spectrum of sodium and of lithium gave spacings characteristic of a centre-faced cubic lattice with 2·03, that is, two atoms per elementary cube.

The five metals are all lustrous, and they tarnish at once on exposure to air owing to the formation of a surface film of oxide. Lithium changes the most slowly, cæsium the most quickly. The metals are therefore preserved in well-stoppered vessels, or immersed in a liquid containing little or no oxygen—*e.g.* water-free ether, naphtha, or petroleum. In order to obtain the silvery-white sodium, etc., the metal is distilled in a stream of hydrogen, and the glass tube immediately sealed. M. Rosenfeld[3] recommends cleaning the crusted alkali metal by immersing it in a mixture of amyl alcohol with three parts of petroleum and rubbing it with a rag soaked in the same mixture until the surface has become silvery-white; the metal is then placed in petroleum containing 5 per cent. of amyl alcohol, washed in petroleum, and finally preserved in a soln. of petroleum with 0·5 to 1·0 per cent. of amyl alcohol. W. Vaubel says that sodium can be kept a long time in vaseline without forming a surface crust. The metal retains its lustre under petroleum only when no oxygen is present. Acid products are present in petroleum, and these form a crust with sodium; it is said that this can be prevented by shaking the petroleum with potash-lye, or by distilling it in a stream of hydrogen or carbon dioxide.

The fractured surface of potassium shows brilliant facets. According to C. E Long,[4] when potassium or sodium is melted in a glass tube in an atm. of coal gas, and the fluid portion poured from the partially congealed mass, octahedral crystals belonging to the tetragonal system are formed; but, according to F. Schœdler, the crystals—*e.g.* sublimate—are usually cubes, belonging to the cubic system. Crystals of sodinm can be obtained by sealing up the metal with hydrogen under reduced press. in a glass tube fitted in the interior with some wire gauze at a constriction in the middle of the tube. The sodium is melted at one end of the tube and filtered through the wire gauze. The tube is then sealed off at the constriction. The metal is melted, allowed to congeal partially, and the interior liquid portion suddenly run away from the solid by turning the tube. According to G. S. Newth, a thin layer of rubidium between two plates of glass is indigo blue; potassium appears bluish-violet; lithium, dark reddish-brown; and sodium, yellowish-brown; while W. L. Dudley[5] found that the vapour of potassium at its b.p. has a greenish colour, and at a red heat, bluish-violet; the vapour of sodium in thin layers appears colourless, in thick layers purple-red, and at higher temp. yellow; while the vapour of rubidium is blue with a greenish tinge. According to E. Linnemann, the oxidation of sodium at ordinary temp. is accompanied by a greenish phosphorescence;[6] and if, when the phosphorescence has ceased, the metal be heated to 60° or 70°, the phosphorescence reappears. An analogous phenomenon occurs when sodium acts on water in darkness. The bluish-white streak which sodium makes on paper shows a green phosphorescence which persists longer than the greyish-white streak made by potassium because sodium is not so rapidly oxidized as potassium.

Different numbers have been reported for the **specific gravities**[7] of the alkali metals, presumably owing to the presence of impurities, as well as to differences of temp. The best representative values at 20° are as follows:

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Sp. gr., solid (20°) . .	0·543	0·9723	0·859	1·525	1·903
At. vol.	13·1	23·7	45·5	56·0	71·0
Expansion on melting .	1·51	2·57	2·60	1·657	1·393 per cent.

The metals lithium, sodium, and potassium are thus lighter than water. Lithium is specifically lighter than any other element solid at ordinary temp.; it floats on

petroleum. According to G. Vicentini and D. Omodei, solid sodium at its m.p. 97·8° has a sp. gr. 0·9519, and liquid sodium, 0·9287; solid potassium at its m.p. 63·5°, 0·851, and liquid potassium, 0·8298. Sodium at its b.p. has a sp. gr. 0·7414; and at the temp. of liquid air 1·0066. Potassium is specifically lighter than sodium, and has nearly twice its at. vol. The at. vol. of cæsium is larger than that of any known element. K. F. Slotte estimated the edge of the molecular cube of liquid and solid sodium and potassium to be respectively $8·7\times10^{-9}$ cm. and $10·7\times10^{-9}$ cm. It is of historical interest to note that in 1808 H. Davy determined the sp. gr. of sodium by finding the proportions of oil of sassafras and naphtha to be mixed to produce a liquid in which the metal remains suspended without sinking or floating. This, said W. Ostwald, shows that H. Davy discovered the method of finding the sp. gr. of solids by suspension, a method attributed by J. W. Retgers to A. Dufour.

Hardness.—The mineralogist defines hardness as the resistance which a body offers to the penetration of points or edges, and when one body A scratches another body B, then A is said to be harder than B. A series of bodies A, B, C, ..., is arbitrarily arranged so that A scratches B, B scratches C, ..., and not conversely. It is assumed that if a point or edge of A scratches a plane surface of B, then a point or edge of B will not scratch a plane surface of A. Taking a hint from R. J. Haüy, F. Mohs devised an arbitrary scale of hardness: talc, 1; gypsum, 2; calcite, 3; fluorspar, 4; apatite, 5; felspar, 6; quartz, 7; topaz, 8; corundum, 9; diamond, 10. A hardness represented by the number 6 means that it can be scratched by bodies above it in the series, and scratch bodies of hardness below it in the series. H. Behrens made the scale more even and regular by using a series of alloys. F. Auerbach prepared fourteen samples of Jena glass of different degrees of hardness, and found that any one variety could be scratched by the other; and he therefore showed that if resistance to scratching be accepted as a definition of hardness, then, of two samples of glass, that is the harder which makes the deeper scratch on the other, when the test is made under like conditions.

E. Winkler, F. Grashof, H. Hertz,[8] etc., have studied the stresses which are set up when two elastic isotropic bodies are in contact over a portion of their surface, when the surfaces of contact are perfectly smooth, and when the press. exerted between the surfaces is normal to the plane of contact. H. Hertz showed that there is a definite point in such a surface representing the hardness defined as the strength of a body relative to the kind of deformation which corresponds to contact with a circular surface of press.; and that the hardness of a body may be measured by the normal press. per unit area which must act at the centre of a circular surface of press. in order that in some point of the body the stress may first reach the limit consistent with perfect elasticity. If H be the hardness of a body in contact with another body of a greater hardness than H, then for a circular "surface of pressure" of diameter d; press. p; radius of curvature of the line ρ; and the modulus of penetration E,

$$H=\frac{6}{\pi}\cdot\frac{p}{d^2};\quad\text{or}\quad H=\frac{1}{\pi}\sqrt[3]{\frac{3}{2}\cdot\frac{E^2p}{\rho^2}}$$

The resistance to penetration defined in this sense is called by F. Auerbach the *absolute hardness* of a body, and he has designed an apparatus for measuring this property.

While hardness may be regarded as the resistance which a body offers to penetration, the resistance is largely determined by the nature of the applied stress. There is the resistance which a body offers to the abrasion of, say, a sand-blast; the resistance it offers to a press.; the resistance it offers to a cutting tool; resistance to deformation, etc. Accordingly, there is a scratching hardness, an abrasion hardness, a cutting hardness, an elastic hardness, a tensile hardness, etc. The usual tests of hardness are static in character, but with kinetic tests, the penetrating body is moving with an arbitrarily assigned speed. As a result, numerous definitions of hardness have been proposed, and numerous instruments have been designed

for measuring hardness—*e.g.* T. Turner's and A. Martens' sclerometers;[9] A. F. Shore's scleroscope; J. A. Brinell's indentation test; W. J. Keep's drill test, etc. In T. Turner's instrument the load required to make a pointed diamond cut a scratch of given width is measured; in A. Martens' instrument, the width of the scratch with a definite load is measured; in J. A. Brinell's apparatus, a hard steel ball (say 10 mm. diam.) is forced into the smooth surface to be tested, and the depth of the indentation measured; the quotient obtained by dividing the press. in k.grm. by the spherical area of the cavity in sq. mm. is taken as a measure of the hardness. P. Ludwik used a steel cone in place of J. A. Brinell's ball. According to N. S. Kurnakoff and S. F. Schemtschuschny, Brinell's hardness number is really a measure of the plasticity of a metal. A. F. Shore's scleroscope measures the rebound of a hard body dropped from a given height on to the surface to be tested, T. A. Jagger and H. C. Boynton used a drill with a diamond point, and W. J. Keep's hardness-testing machine measures the number of revolutions required to make a drill with a definite load cut a hole to a definite depth. A. Kürth, R. P. Devries and A. F. Shore, and R. Guillery measure hardness in terms of the tensile strength or the lower elastic limit of a metal, for, as C. Karmarsch showed, the harder a metal the greater its tensile strength.

Just as the press. of a gas, at a given temp., is proportional to the number of mols. in unit space, so, with a homogeneous solid, it might be assumed that the resistance it offers penetration by another body will increase as the number of atoms in unit volume increases, and accordingly, S. Bottone[10] was led to postulate that hardness varies inversely as the at. vol.; and it is found generally that soft metals have a large at. vol. and hard metals a small at. vol. For example, with S. Bottone's scale of hardness:

Hard metals.			Metals of medium hardness.			Soft metals.			Very soft metals.		
	At. vol.	H.		At. vol.	H.		At. vol.	H.		At. vol.	H.
Ni .	6·7	1410	Ir .	8·6	984	Al .	10·6	821	Na .	23·7	400
Co .	6·9	1450	Pd .	8·9	1200	Cd .	12·9	760	K .	45·4	230
Mn .	6·9	1456	Zn .	9·1	1077	Mg .	13·8	726	Rb .	55·8	—
Fe .	7·2	1375	Pt .	9·1	1107	Sn .	16·1	651	Cs .	71·0	—
Cu .	7·2	1360	Au .	10·2	979	Th .	17·3	565	Ca .	36·6	405
Cr .	7·7	—	Ag .	10·2	990	Pd .	18·1	570	Sr .	35·1	—

Allowing for variations in the hardness due to impurities, it therefore appears that hardness measures the resistance offered by the mols. of a substance to their separation by the penetration of another substance. G. A. Kenngott, A. Schrauf, C. Benedicks, and J. L. C. Schroeder van der Kolk have also tried to establish empirical relations between hardness and other physical properties of the elements. It follows that if hardness varies inversely as the at. vol.—or atom conc.—the curve obtained by plotting the hardness of the elements against the at. wt. will exhibit a periodic character like the at. wt.-at vol. curve; and this was shown to be the case by J. R. Rydberg, in the curve illustrated in Fig. 10. C. A. Edwards also

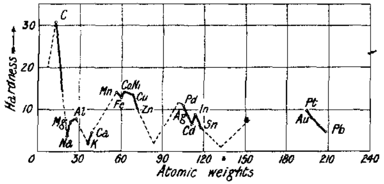

Fig. 10.—Periodic Curve showing the relation between the Hardness and Atomic Weight of the Elements.

found the hardness of the solid elements to be a periodic function of the at. wt.; and that while there is a close connection between the hardness and at. vol. curves there is an even closer parallelism between the hardness and absolute m.p. curves. Practically, all the changes in the m.p. curves are reflected by corresponding changes in the hardness.

The hardness of a metal is greatly influenced by the presence of small amounts of other elements. N. S. Kurnakoff and S. F. Schemtschuschny have shown that when two metals unite to form a solid soln. there is a continuous series of mixed crystals, the curve of hardness is a continuous one which passes through a maximum, and this point of maximum hardness generally corresponds with that of minimum electrical conductivity. When the metals form alloys which solidify as a mechanical mixture of two components the hardness curve is approximately a straight line. When the metals form only a limited series of mixed crystals the curve of hardness is a combination of the two forms previously mentioned; while, lastly, if the two metals form a definite chemical compound this may be either harder or softer than the constituents. Again, in passing from either end of a series of solid solns. towards the centre of the series, it will be found that the hardness, the limit of elasticity, and the tensile strength increase, but the ductility (as measured by the extension and the reduction of area) and the electrical conductivity decrease. The m.p. usually changes fairly regularly throughout the series. The facts are illustrated diagrammatically in Fig. 11. A. Kürth showed that with the non-ferrous metals—copper, silver, nickel, aluminium, zinc, and tin—the hardness decreased as the temp. rose, but with annealed steels—0·2 to 0·75 per cent. carbon—the hardness decreased as the temp. rose to 150°; increased a little from 150° to 250°; and decreased between 250° and 500°. C. A. Edwards gave 0·07 for Brinell's hardness of sodium, and 0·04 for that of potassium.

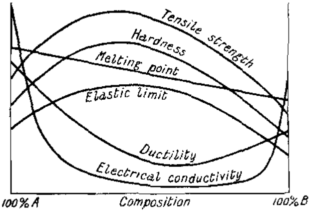

FIG. 11.—Relation between Hardness and other Physical Properties of Solid Solutions (Diagrammatic).

Sodium at 50° is soft, and at ordinary temp. it may be squeezed with the fingers, at 0° it is very ductile, and at −20° it is hard.[11] Lithium is harder than sodium or potassium, but it can be scratched by lead, drawn into wire, or rolled into thin plates. Potassium is harder than sodium, but it can be scratched by lithium, lead, calcium, and strontium. Cæsium is one of the softest of metals, rubidium comes next; at −10° rubidium is as soft as beeswax. N. Slatowratsky and G. Tammann[12] tried to find if crystals of potassium and sodium soften in the neighbourhood of their m.p. by heating them under a load near their m.p. Under a press. of 27·5 kilograms per sq. cm. the depression 2° below the m.p. was 48 units for potassium and 60 units for sodium; 5° below the m.p. the depression was respectively 8·3 and 36; 10°, 7·7 and 24 units; and 15°, 7 and 18 units. C. A. Edwards gives 0·07 and 0·037 respectively for the Brinell's hardness numbers of sodium and potassium. According to J. R. Rydberg,[13] the **relative hardness** of the alkali metals at ordinary temp. is indicated in the following table, which also includes T. W. Richards' values at 20° for the average **compressibilities**, β, of the alkali metals for press. between 100 and 500 megabars. The values of β represent the average fractional changes of vol. caused by one megabar press. between 100 and 500 megabars referred to the volume v_0 of the uncompressed substance—$dv/(v_0dp)$. Mercury, the standard of reference, has β=0·00000395 megabars at 20°.

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Relative hardness . .	0·6	0·4	0·5	0·3	0·2
Compressibility, β . .	0·000009	0·0000156	0·0000317	0·000040	0·000061

The compressibility of cæsium is very high, and appears to be connected with the high at. vol. of this element. The change of volume [14] of potassium at atm. press. is 0·02680 c.c. per grm., and of sodium, 0·02787 ; at 1000 kilogrm. per sq. cm. press., 0·02368 c.c. for potassium and 0·02555 c.c. for sodium ; at 6000 kilogrm. per sq. cm. press., 0·01347 c.c. for potassium and 0·01873 for sodium ; at 12,000 kilogrm. per sq. cm. press., 0·00642 for potassium and 0·01398 for sodium. The **surface tension** of molten sodium in an atm. of carbon dioxide and at a temp. slightly above its m.p. is 25·75 mgrm. per mm. according to G. Quincke,[15] and 27·23 mgrm. per mm. according to E. B. Hagen. The surface tension of sodium at 90° in an atm. of carbon dioxide is 293·6 dynes per cm. ; and of potassium, at 62°, 411·5 dynes per cm. The sp. cohesion—$a^2=2a/S$, where S denotes the sp. gr. of water and a the surface tension—is 64·4 per sq. mm. for sodium and 101·1 for potassium. M. von Wogau found the **rates of diffusion** of the alkali metals in 0·1 per cent. mercury amalgams are : lithium at 8·2°, k=0·66 ; sodium at 9·6°, k=0·64 ; potassium at 10·5, k=0·53 ; rubidium at 7·3°, k=0·46 ; cæsium at 7·3°, k=0·15, where k denotes the quantity of substance (mol. per litre) which passes per sq. cm. between two planes 1 cm. apart with unit difference in conc. on the two planes, per day. W. Wenz found the **velocity of sound** in the vapour of potassium at 850° to be 652 metres per sec.

The **melting points** of the metals, reported by different investigators, vary somewhat owing probably to differences in the purity of the specimens used for the determination.[16] The best representative values are indicated in Table III. According to P. W. Bridgman, the effect of press. in kgrm. per sq. cm. (1 atm. =1·033 kgrm. per sq. cm.) on the m.p. θ of potassium and sodium is as follows :—

Press.	1	1000	2000	4000	6000	8000	10000	12000
Na θ	97·6°	106·2°	114·3°	129·1°	142·9°	155·0°	166·6°	177·2°
Na $d\theta$		8·6°	8·1°	7·4°	6·7°	6·2°	5·8°	5·3°
K θ	62·5°	78·7°	92·4°	115·8°	135·4°	152·2°	166·7°	179·5°
K $d\theta$		16·2°	13·7°	11·7°	9·8°	8·4°	7·2°	6·4°

According to G. Tammann, the m.p., θ°, of potassium is $\theta=59·5+0·0146p+0·0000007p^2$. The changes in volume of the liquid dv_l/dT and of the solid, dv_s/dT at the m.p. are respectively 0·000299 and 0·000216 for sodium, and 0·000360 and 0·000276 for potassium. P. W. Bridgman found the effect of press., p, in kgrms. per sq. cm., on the m.p., θ°, of lithium to be

p	0	1000	3000	5000	7000	8000
θ	178·4°	182·1°	188·8°	194·6°	199·4°	201·6°

The results are thus characteristic of a liquid which contracts on freezing ; and the mean value of the increase in vol. on melting is 0·006. The **boiling points** of the elements also vary considerably.[17] The best representative values are indicated in Table III. Lithium volatilizes at a bright red heat. According to A. Gebhardt, the **vapour pressure** of sodium at

	380°	420°	480°	520°	540°	550°	560°	570°
Vap. press.	1·2	2·0	6·1	12·4	18·5	23·0	32·2	80·2 mm.

and, according to F. Krafft and L. Bergfeld, sodium boils in the vacuum of the cathode light at about 140°, and potassium at about 90°. G. Bartha gave for the b.p. of the metals in the cathode light : 575°, lithium ; 420°, sodium ; 370°, potassium ; 355°, rubidium ; and 315°, cæsium. A. Kröner calculated the vapour pressure of lithium to be

	630°	731°	765°	799°	867°	900°	1000°
Li	0·05	0·60	1·0	1·7	3·7	5·5	760 mm.

A. Kröner gave for potassium and cæsium

	249·5°	288·0°	327·2°	336·0°	355·5°	381·5°	398·6°
Cs	0·31	1·34	3·61	4·49	6·65	—	15·88 (397°)
K	0·05	0·21	0·73	0·95	1·51	2·84	4·01

The value for cæsium at 397° is by L Hackspill, who also obtained values for sodium, potassium, cæsium, and rubidium, and for the latter he gave

	250	292°	305	330	340	353	360
Rb . .	0·06	0·98	1·46	2·66	3·29	4·25	—

The **latent heat of fusion** [18] per gram is indicated in Table III along with the best representative values for the m.p. and b.p. E. Griffiths found the latent heat of fusion of sodium to be 27·1 cals. per gram; I. Iitaka gives 2·60. A. Thum gave 32·81 grm. cals. for lithium. E. Rengade gave for the heat of fusion of sodium 27·21; potassium, 14·67; rubidium, 6·144; and cæsium, 3·766. Trouton's ratios of the atomic heat of fusion to the absolute m.p. are respectively 1·69, 1·70, 1·68, and 1·66. P. W. Bridgman found the latent heat of potassium changed from 5·51 kilogrammetres per gram to 5·81 at 1000 kilogrms. per sq. cm., while the corresponding values for sodium changed from 12·90 to 12·46; there is a maximum of 6·22 with potassium at 4000 kilogrm. per sq. cm. press., and a minimum of 11·93 with sodium at the same press.; the value for potassium at 12,000 kilogrms. per sq. cm. press. is 4·83, and with sodium 12·72 kilogrammetres per grm. The **specific heats** [19] are indicated below. The sp. ht. of sodium from

TABLE III.—HEAT CONSTANTS FOR THE ALKALI METALS.

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
M.p. .	180°	97·6°	63·5°	39°	28·5°
B.p. . .	+1400°	877·5°	759°	696°	670°
Heat of fusion per grm. .	—	27·21	14·67	6·144	3·766 Cals.
At. ht. of fusion .	0·941	0·9811	0·1728	0·0802	0·0522
Entropy at 25°	7·6	12·2	19·7	—	—

−191° to −83°	*−79·5° to 17°*	*0° to 20°*	*to 56·5*	*to 78°*	*to 97·63°*	*to 100°*	*to 157°*
0·2433	0·2830	0·2970	0·3071	0·3191	0·3290	0·3330	0·3330

and for potassum from

−191° to −80°	−78·5° to 0°	0° to 22·3°	to 56·5°	to 62·04°	to 78°	to 100°	to 157
0·1568	0·1662	0·1876	0·1922	0·1980	0·2137	0·2170	0·2245

The sp. ht. of rubidium between 20° and 35° is 0·07923, and of cæsium from 0° to 26°, 0·04817. I. Lämmel's value for lithium at the m.p. (193°) is 1·3; and for sodium at the m.p. (100°) is 0·35. E. D. Eastman and W. H. Rodebush's value for the **atomic heats** of sodium at the absolute temp. T is

T° K. . . .	64·6°	71·1°	84·6°	156·8°	181·7°	234·7°	293·5°
C_p	4·52	4·77	5·08	6·02	6·15	6·43	6·79
C_v	4·47	4·71	5·00	5·82	5·91	6·07	6·29

similarly for potasium

T° K. . . .	68·6°	76·0°	87·0°	101·8°	119·3°	199·5°	286·7°
C_p	5·76	6·78	5·96	6·06	6·23	6·72	7·10
C_v	5·69	5·70	5·86	5·95	6·07	6·37	6·52

For each metal, therefore, the at. ht. C_v rises well above the normal value 6. For potassium at the m.p. L. Protz gave for the atomic heat of the solid C_p=7·81, and C_v=7·26; and of the liquid, C_p=7·96, and C_v=7·25; similarly, E. Griffiths gave for solid sodium C_p=7·49, and C_v=6·71; and for liquid sodium, C_p=7·43.

and C_v=6·61. P. Günther measured the sp. ht. of sodium between −186° and −149°, and found the results agreed with those calculated by P. Debye's formula on the assumption that $\beta\nu$=125. A. Bernini measured the sp. ht. of sodium and potassium; and A. Thum that of sodium and of lithium. The latter gave for sodium 0·1743 at −273°, and 0·3369 at 150°. E. Rengade gave for the sp. ht. of solid sodium 0·2811+0·000233θ and for the liquid 0·330 at 98°; for solid potassium, *0·1728+0·000142θ, and for the liquid 0·1422+0·000668θ; for solid rubidium,* 0·0802+0·000153θ, and for the liquid 0·092+0·000668θ; and for solid cæsium, 0·0522+0·000137θ, and for the liquid 0·0604−0·000034θ. J. Dewar found that between the b.p. of hydrogen and nitrogen—about −223°, or 50° K.,

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Sp. ht. . .	0·1924	0·1519	0·1280	0·0711	0·0513
At. ht. . .	1·35	3·50	5·01	6·05	6·82

R. Lämmel found the at. ht. of lithium rises to 9·45 at the m.p. 193°; and that of sodium to 8·23 at its m.p. The at. ht. of sodium rises from 6·5 at 0° to 7·5 at 96°—the theoretical limiting value at constant volume is nearly 6, which is lower than the value calculated from the formula $C_p-C_v=a^2Tv/\beta$. I. Iitaka gives for the sp. ht. of solid sodium at its m.p. 0·330, and of the liquid at the same temp., 0·347, and the respective at. hts. are 7·59 and 7·98. A. Joannis gives for the sp. ht. of solid potassium 0·166, and of the liquid 0·25. W. Nernst obtained the relation $C_2-C_3=Q/T_m$, where C_2 and C_3 respectively denote the mol. ht. of liquic and solid at the m.p., T_m the absolute temp. of the m.p., and Q, the latent heat of fusion. I. Iitaka found the relation is not good with the metals bismuth, tin, mercury, zinc, lead, and sodium, and also with sulphur for the quotients are respectively 4·71, 3·15, 2·40, 2·19, 1·19, 1·61, and 1·08. A. Thum gave for lithium,

	−273°	−200°	−100°	−50°	0°	50°	150°	180°
Sp. ht. .	0·5303	0·5890	0·6809	0·7315	0·7854	0·8425	0·9658	1·0055
At. ht. .	3·7121	4·1230	4·7663	5·1205	5·4978	5·8971	6·7606	7·0385
At. ht. .	(0·9086)	(2·5837)	(4·1965)	(4·8755)	(5·5657)	(6·3441)	(8·4539)	(9·3163

The numbers in brackets are by R. Lämmel.[20] The sp. ht. of lithium is the largest of that of all the elements. R. Lämmel represents the sp. ht. of lithium at θ° by the expression 0·7951+0·0020632θ+0·0000025080θ^2+0·0000000014207θ^3. The observed values are 0·3693 at −200°; 0·5997 at −100°; 0·6964 at −50°; 0·7951 at 0°; 0·9063 at 50°; 1·0407 at 100°; and 1·3745 at 190°, so that the sp. ht. curve shows a slight turning-point at about −60°, Fig. 12, possibly corresponding with a change from one allotropic form **α-lithium** to another form **β-lithium.** The sp. ht. of sodium was found by E. Griffiths to increase with temp., but its absolute value at any given temp. depends on the previous thermal treatment of the metal. At temp. below about 60°, the sp. ht. is greater when cooled by quenching than when annealed.

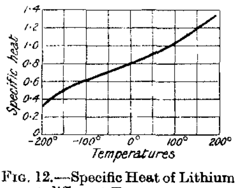

FIG. 12.—Specific Heat of Lithium at different Temperatures.

The sp. ht. of liquid sodium varies with temp. such that the temp. coeff. is −0·00034 per degree; I. Iitaka found very little variation in the at. ht. of solid and liquid at the m.p. Hence, E. Cohen and G. de Bruin argue that under ordinary conditions two allotropic modifications—**α-sodium** and **β-sodium**—are present in proportions dependent upon its previous thermal treatment. The transition point not yet determined lies between 0° and 90°—possibly it is near 75°. *Dilatometric measurements show that the high temp. β-form has the lower* density; and since the rapidly quenched metal melts more quickly than the slowly cooled metal, it is inferred that the change from the α- to the β-form is attended by the evolution of heat. Similar observations show there are two allotropic

forms of potassium—**α-potassium** and **β-potassium**—with a transition point in the neighbourhood of 59·7°. W. Holt and W. E. Sims [21] found that potassium is ductile and soft at 54·5°, but it becomes quite brittle and has a conchoidal fracture at 60·5°.

The best representative values of the varied measurements [22] of the **coefficients of cubical expansion** of the five alkali metals are :

Lithium.	*Sodium.*	*Potassium.*	*Rubidium.*	*Cæsium.*
0·000190	0·000274	0·000283	0·000338	0·000338

The coeff. of expansion of sodium between 0° and 95° is uniform and proportional to the temp., and the coeff. is greater for the liquid than for the solid. According to A. Bernini and C. Cantoni, unit volume of the metal at 0° occupies v volumes at $\theta°$, when $v=1+a\theta+\beta\theta^2$. The values of the constants for the liquid and solid metals are indicated in Table IV. A. Thum's value for lithium is 0·0001801.

TABLE IV.—COEFF. OF THERMAL EXPANSION OF THE ALKALI METALS.

	Temp. interval.	a	β
Lithium—solid . . .	0°–178°	0·0001535	0·000000092
liquid . .	182°–235°	0·0001743	0·000000106
Sodium—solid . . .	0°–78°	0·0001816	0·000000280
liquid . .	100°–235°	0·0002599	0·000000286
Potassium—solid . .	0°–56°	0·0002112	0·000000155
liquid . .	78°–235°	0·0002681	0·000000210

Potassium and sodinm are good **conductors of heat.**[23] If the conductivity of silver be unity, that of sodium is 0·365. J. W. Hornbeck found the temp. coeff. of the thermal conductivity of potassium or sodium falls with rise of temp. The alkali metals are also good conductors of electricity ; [24] for example, the conductivity of sodium for heat and electricity is exceeded only by silver, copper, and gold. According to E. F. Northrup, the metals sodium, potassium, mercury, tin, lead, and bismuth have the same value for the ratio of the coeff. of electrical resistance to the coeff. of cubical expansion at the same temp. The **electrical conductivity** of lithium is nearly $11·4\times10^4$ reciprocal ohms at 20°, that is, about 20·4 per cent. of the conductivity of hard silver ; of sodium at 21·7°, $22·4\times10^4$ reciprocal ohms, that is, about 36·5 per cent. of the value of silver.

Between	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
−178° and −190°	$74·6\times10^4$	125×10^4	$51·0\times10^4$	40×10^4	$19·1\times10^4$
−178° and −78·3°	$18·5\times10^4$	35×10^4	$23·3\times10^4$	$15·9\times10^4$	$7·8\times10^4$
0°	$11·7\times10^4$	$22·3\times10^4$	$14·3\times10^4$	$8·6\times10^4$	$5·18\times10^4$

The value for solid lithium is $7·88\times10^4$, and for the liquid $2·21\times10^4$ at 230°. Solid sodium $18·8\times10^4$ at 50° ; $9·8\times10^4$ at 116° ; and $11·42\times10^4$ at 120° for the liquid. Solid potassium $11·6\times10^4$ at 50° ; $6·29\times10^4$ for the liquid at 100°. Solid rubidium $8·34\times10^4$ at 18° ; $5·10\times10^4$ for the liquid at 40°, and $4·78\times10^4$ at 43°. Solid cæsium $4·74\times10^4$ at 19·3° ; $2·73\times10^4$ for the liquid at 30° ; and $2·70\times10^4$ at 37°. The **electrical resistance of solid** lithium at a temp. $\theta°$ between 0° and 177·8° is $R_0(1+0·004568\theta)$ and for the liquid between 177·8° and 230°, $R(1+0·002729\theta)$, when R is the electrical resistance in ohms at 0° ; for sodium from 0° to 97·3°, $R(1+0·004386\theta)$, and from 98·5° to 120°, $R(1+0·003328\theta)$; for solid potassium from 0° to 61°, $R(1+0·00581\theta)$, and for the liquid from 62·5° to 130°, $R(1+0·004184\theta)$. A. Matthiessen's value for the ratio of the resistance of liquid : solid is 1·35 for sodium, and 1·36 for potassium. J. W. Hornbeck found that the temp. coeff. of the resistance of potassium and sodium are high ; and that the ratio of the thermal to the electrical conductivity is exceptionally high. B. Gudden and R. Pohl measured

the electrical conductivity of phosphorescent sodium under a field strength of 16,000 volts per cm. With lithium for press., p, in kgrms. per sq. cm., the electrical resistance is as follows—the liquid state is indicated by an asterisk:

	p	0	1000	3000	5000	7000	9000	12000
Li	0°	1·000	1·0069	1·0212	1·0360	1·0514	1·0675	1·0927
	50°	1·2122	1·2206	1·2379	1·2558	1·2745	1·2940	1·3246
	100°	1·4580	1·4681	1·4889	1·5105	1·5329	1·5564	1·5932
Na	0°	1·0000	0·9376	0·8348	0·7550	0·6922	0·6422	0·5854
	100°	2·2381*	1·4257	1·2451	1·1123	1·0118	0·9320	0·8425
	200°	3·0725*	2·808*	2·397*	2·092*	1·857*	1·670*	1·464
K	0°	1·128	0·941	0·692	0·554	0·458	0·387	0·310
	95°	2·387*	1·911*	0·880	0·693	0·564	0·463	0·350
	165°	3·040*	2·568*	1·853*	1·374*	1·050*	0·829*	0·389

The press. coeff. of potassium and sodium increase with rising temp. and decrease with rising press.; while the temp. coeff. of the resistance decrease with increasing press., and more so with potassium than with sodium; with lithium, the press. coeff. increases with rising press., and falls with rise of temp., while the temp. coeff. falls with increasing press. P. W. Bridgman found the sp. resistance of liquid lithium to be 1·68 times that of the solid at the m.p. (178·4°) at atm. press. A. Bernini found 2·51 at the m.p. (177·84°); for sodium, A. Bernini found 1·337, E. F. Northrup, 1·44, and P. W. Bridgman, 1·451; and for potassium, A. Bernini found 1·392, E. F. Northrup, 1·53, and P. W. Bridgman, 1·56. In comparing these ratios, A. Matthiesen showed that errors are likely to occur in the results for the solid state because of the strains and of cavities formed during freezing. The **thermoelectric force** [25] of sodium towards platinum at 100° is —0·21 millivolt; and —0·94 millivolt for potassium. The **magnetic susceptibility** [26] of potassium between 18° and 180° is $+0·40\times10^{-6}$ per unit mass; for sodium, $+0·51\times10^{-6}$; and for lithium, $+0·38\times10^{-6}$.

The electro-affinity of lithium is smaller than that of any of the other alkali metals, and it exhibits a greater tendency than the other alkali metals to form complex salts—*e.g.* the solubility of ammonia in water is raised by the addition of a lithium salt, which presumably unites with the ammonia; the solubility curves of the lithium salts in water usually show more breaks than the corresponding salts of the other alkali metals owing to the formation of hydrates. Potassium, rubidium, and cæsium seem to have a smaller and smaller tendency to form complex salts as the at. wt. of the element increases; otherwise expressed, the electro-affinity, or the ionization tendency of the alkali metals increases as the at. wt. increases. This is illustrated by the heats of ionization. According to W. Ostwald,[27] the **heat of ionization** per gram-atom is

Lithium.	Sodium.	Potassium.	Rubidium.
+62·9	+57·4	+62·0	+62·6

Meaning that with sodium: $Na=Na^{\cdot}+57·4$ Cals., etc. The alkali salts are ionized in aq. soln., and behave generally like strong electrolytes. The ionization factor with soln. containing 2 per cent. of lithium chloride varies from 1·70 to 2·0 when determined by the lowering of the vap. press. or f.p.; the raising of the b.p.; or by the mol. conductivity. Similar remarks apply to the salts of the alkali metals. K. Fajans [28] calculates the **heat of hydration of ions** to be $H^{\cdot}$, 362; $Li^{\cdot}$, 210; $Na^{\cdot}$, 203; $K^{\cdot}$, 182; $Rb^{\cdot}$, 173; $Cs^{\cdot}$, 174 kgrm. cal. per gram-ion. R. Lorenz and P. Walden found the **diameters of the ions** of lithium, sodium, and potassium in aq. soln. to be respectively $4·52\times10^{-8}$, $3·48\times10^{-8}$, and $2·34\times10^{-8}$ cm., and in methyl alcohol soln., $9·40\times10^{-8}$, $7·04\times10^{-8}$, and $4·98\times10^{-8}$ cm. The **diameters of the atoms** are respectively $2·01\times10^{-8}$, $2·52\times10^{-8}$, and $3·14\times10^{-8}$ cm.

According to W. Ostwald and G. Bredig, the transport number of complex ions usually decreases with an increase in the number and mass of atoms forming the complex, but with the alkali metals, the **transport numbers** of the ions at 18°

increase with an increase in the at. wt. of the ions. For instance, at 18°, the transport numbers of the ions of the alkali metals and the **absolute velocity of the ions,** with a difference of potential of one volt per centimetre, expressed in centimetres per second, are indicated in the following table along with the temp. coeff. of the transport numbers at 18° :

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Transport number .	33·4	43·6	64·7	67·6	68·2
Temp. coeff. . .	0·0265	0·0244	0·0217	0·0214	0·0212
Absolute velocity . .	0·000346	0·000452	0·000680	0·000700	0·000707

According to F. Kohlrausch,[29] these anomalous results are not due to the friction between the elementary ions and the water mols., but rather to the friction between the water mols. and complexes—hydrated ions. The absolute velocity of transport of the ions is calculated by dividing the transport numbers by 96540, the electric charge carried by the transported ions. Lithium salts are also strongly ionized in many non-aqueous solns.—*e.g.* methyl or ethyl alcohol. P. Lenard and co-workers calculate the number, n, of molecules of water combined with the ions in aq. soln., and, r, the radius of the ions :

	$Li^{\cdot}$	$Na^{\cdot}$	$K^{\cdot}$	$Rb^{\cdot}$	$Cs^{\cdot}$
n . . .	19	12	7	6	6
$r \times 10^8$.	5·0	4·2	3·1	2·9	2·8 cm.
Q . . .	110	103	82	78	74 Cals.

R. Lorenz, P. Walden, and K. Fajans and K. F. Herzfeld have also made estimates of the diameters of these ions in aq. and non-aq. solvents. M. Born's estimated values Q for the heats of hydration of the ions are indicated above.

The **electrolytic potential** of lithium is −2·7 ; of sodium, −2·8 ; and of potassium, −3·2 volts, meaning in a normal soln. of, say, a sodium salt, the potential towards sodium is 2·8 volts less than the potential of a platinum electrode sat. with hydrogen at atm. press., immersed in a normal acid soln. ; or the electromotive force of the cell Na | N—$Na^{\cdot}$ | N—$H^{\cdot}$ | H_2Pt is 2·8 volts with sodium as cathode. These cells are not always realizable. The electrode potential of the alkali metal in normal soln. against a normal calomel electrode is 3·3044 volts for lithium, 2·9981 volts for sodium, and 3·2084 volts for potassium.[30] G. N. Lewis and co-workers found for the potential of the alkali metals against a normal calomel electrode, Li, 3·305 volts ; Na, 2·993 volts ; K, 3·203 volts ; and Rb, 3·305 volts. According to M. N. Saha, the **ionizing potential** of sodium vapour is 5·12 volts or $1·17 \times 10^5$ cals. ; potassium vapour, 4·318 volts or $1·00 \times 10^5$ cals. ; rubidium vapour, 4·16 volts or $0·96 \times 10^5$ cals. ; and cæsium vapour, 3·88 volts or $0·90 \times 10^5$ cals.

A. Campetti[31] concludes from his experiments that in darkened unsaturated sodium vapour, freed from the electrons emitted from the surface of the fused metal, ionization takes place spontaneously and that the absorption of the D-line is strictly related to the conductivity of the vapour. Further, when absorption is observed in sodium vapour below 400°, it is probably the result of electrons from the surface of the fused metal, or from a photoelectric action on the atoms of sodium vapour. The emitting or absorbing vibrations in sodium vapour with respect to the D-line are those of positive-ion-atoms.

R. Pohl and P. Pringsheim[32] located a selective maximum **photoelectric effect** with four alkali metals for wave-lengths λ in $\mu\mu$

	Lithium.	Sodium.	Potassium.	Rubidium.
λ . . .	280	340	440	475

K. T. Compton and O. W. Richardson, with isotropic radiation, found a maximum for sodium at $225\mu\mu$ and $360\mu\mu$; and a maximum at $250\mu\mu$ for cæsium. R. A. Millikan and W. H. Souder found that with new surfaces of lithium, sodium, and potassium there are definite maxima for the selective absorption about $250\mu\mu$

for lithium; 350$\mu\mu$ for sodium; and 390$\mu\mu$ for potassium. H. Küster and K. Fredenhagen, and G. Wiedmann and W. Hallwachs believe that pure metal surfaces are not photo-active. J. Braun, and E. F. Seiler studied the photoelectric effect with sodium, potassium, rubidium, and cæsium with light of different wave length.

S. H. Anderson and J. A. Gilbreath inferred that the vapour of potassium at 55° is ionized by exposure to ultra-violet light and by ordinary light because (i) if the beam of light is directed first on one electrode, then on the other, and then midway between the electrodes, the photoelectric currents are nearly the same; (ii) the photoelectric currents decrease when the temp. of the main part of the bulb is raised so as to drive the vapour into the cooler part of the tube; (iii) the photoelectric currents decrease when the vap. press. is decreased by lowering the temp of the bulb; and (iv) the ionization currents have approximately the same magnitude when a positive or negative e.m.f. is applied. These results are not such as would be anticipated if the phenomenon were wholly due to the photoelectric effect of the thin imperceptible layer of potassium condensed on the electrodes. The ionization is increased if a little foreign gas be associated with the vapour of the metal.

T. Svedberg [33] prepared colloidal solns. of the alkali metals in ethyl ether, and he gives Table V showing the colours of coarse and fine ethylethersols, as well as

TABLE V.—COLOURS OF THE ETHERSOLS OF THE ALKALI METALS.

Metal.	Colour of ethylethersols.		Colour of vapour.
	Small particles.	Large particles.	
Lithium	Brown	Brown	—
Sodium	Purple-violet	Blue	Purple
Potassium	Blue	Bluish-green	Bluish-green
Rubidium	Greenish-blue	Greenish	Greenish-blue
Cæsium	Bluish-green	Greenish-blue	—

the colours of the vapours. The stability of the organosol diminishes in passing from sodium to cæsium. The maximum absorption of colloidal sodium, as in the case of gold, changes from yellowish-green to red during coagulation.

The **refractive index** of molten sodium for light of wave-length 589$\mu\mu$ is 0·0045. J. Kanonnikoff [34] has calculated the refractive indices R_c for the C-line, and for infinity, the theoretical limit of the spectrum, R_∞, according to Gladstone and Dale's formula:

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
R_c	3·16	4·22	7·75	12·04	19·55
R_∞	3·00	4·00	7·40	11·60	18·70

Light is partially polarized by reflection from the polished surface of a metal, and plane-polarized light in general becomes elliptically polarized by reflection from such a surface. This was found to be due to the relative change in phase of the two components, which was measured in 1847 by J. Jamin, who thereby calculated the index of refraction of the metal. The so-called *optical constants* [35] of a metal include the refractive index and the **index of absorption** k. The amplitude of a wave of light, after travelling one wave-length λ, measured in the metal, is reduced in the ratio $1 : e^{-2\pi k}$, and, for any distance l, in the ratio $1 : e^{-2\pi lk/\lambda}$. P. Drude found that for liquid sodium, when λ=0·589μ, the index of refraction is 0·04; the index of absorption 2·61; and the reflecting power, 99 per cent. R. W. and R. C. Duncan found that for light of wave-length 665·0, 546·0, and 435·0$\mu\mu$, the respective indices of refraction are 0·051, 0·052, and 0·058, and indices of

absorption respectively 55·0, 42·6, and 31·7 per cent. Similarly for potassium, for light of wave-length 665·0, 589·3, and 472·0$\mu\mu$, the respective indices of refraction are 0·066, 0·068, and 0·070, and the indices of absorption respectively 26·8, 22·1, 14·3 per cent. There is a minimum in the index of refraction curve of sodium very near the *D*-line. J. B. Nathanson found for rubidium, respectively for light of wave-length 640·9$\mu\mu$, 539·6$\mu\mu$, and 454·6$\mu\mu$, the indices of refraction 0·093, 0·093, and 0·091; *k*, 10·51, 7·97, and 5·28; and for the reflecting power, 84, 81·7, and 78·9 per cent. for metal to glass boundary; the reflecting powers were rather lower than for the metal to air boundary excepting in the case of light on small wave-lengths. Metallic sodium, therefore, has the lowest index of refraction and the highest reflecting power of any known metal. M. K. Frehafer measured the reflection and transmission of ultra-violet light by potassium and sodium.

The **spectra** of the alkali metals are illustrated by Fig. 13. A lithium salt in the non-luminous gas-flame furnishes two sharply defined spectral lines, a weak yellow line, Li_β, of wave-length 6104, and a bright red line, Li_α, of wave-length 6708. The presence of nearly a millionth of a milligram of lithium can be detected in this

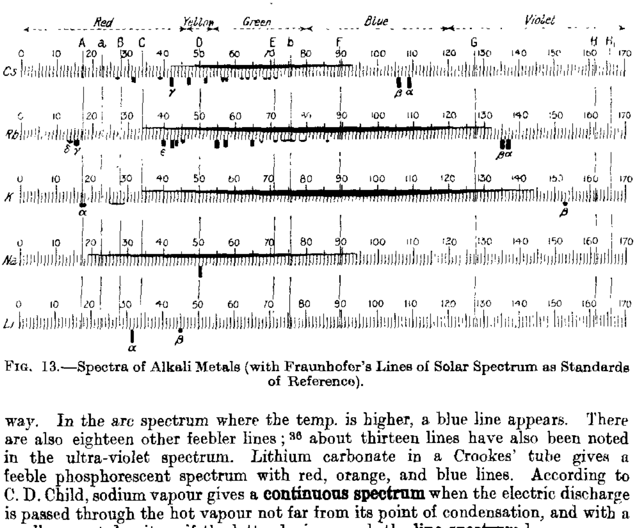

FIG. 13.—Spectra of Alkali Metals (with Fraunhofer's Lines of Solar Spectrum as Standards of Reference).

way. In the *arc* spectrum where the temp. is higher, a blue line appears. There are also eighteen other feebler lines;[36] about thirteen lines have also been noted in the ultra-violet spectrum. Lithium carbonate in a Crookes' tube gives a feeble phosphorescent spectrum with red, orange, and blue lines. According to C. D. Child, sodium vapour gives a **continuous spectrum** when the electric discharge is passed through the hot vapour not far from its point of condensation, and with a small current density; if the latter be increased, the **line spectrum** becomes more pronounced and the *continuous spectrum* less pronounced. If a condenser is in circuit only the line spectrum is alone produced. P. D. Foote and W. F. Meggers deduce a possible structure for the cæsium atom from the spectrum of the element and the ionization potential.

T. Melville noted in 1752 that sodium colours the flame of alcohol yellow, and A. S. Marggraf used this as a test to distinguish sodium from potassium salts. With an ordinary one-prism spectroscope, the spectrum appears with a single yellow line corresponding with the *D-line of the solar spectrum*. *This line really* consists of two lines of wave-length 5896 and 5890. The emission spectrum of sodium shows many other lines of feeble intensity. In a salted Bunsen's flame, practically

no other sodium lines appear. With electrical stimulation, in the vacuum tube other bright sodium lines appear, some in the visible, some in the ultra-violet.

When a sat. soln. of sodium chloride is sprayed into Bunsen's flame, by means of a suitable apparatus [37]—*e.g.* the sprayer of A. Gouy, E. Beckmann and H. Linder, C. de Watteville, etc.—the flame shows two spectra—the brilliant yellow lines, and a continuous spectrum with a maximum in the blue, as observed by G. Kirchhoff and R. Bunsen, A. Gouy, etc. Under ordinary conditions, the yellow lines mask the blue luminescence in the salted Bunsen's flame. There is also a blue or bluish-green luminescence in the flame salted with lithium or potassium chloride, as shown by P. Lenard, but it is usually masked by the more familiar line spectrum. The two spectra seem to be independent. E. Mitscherlich showed that if sufficient ammonium chloride be mixed with sodium chloride, the yellow line spectrum virtually disappears; and that the yellow line spectrum is not produced by sodium chloride in the hydrogen flame burning in chlorine; A. Smithells confirmed this observation, and showed that if oxygen be entirely absent, the yellow colour would probably disappear altogether. C. Fredenhagen found that the faint continuous spectrum of the hydrogen-chlorine flame appears to be intensified when sodium chloride is introduced therein. W. D. Bancroft and H. B. Weiser made analogous observations with respect to potassium, and lithium chlorides, and they add that similar remarks apply to the chlorides of the alkaline earths.

W. D. Bancroft and H. B. Weiser point out that the blue luminescence of sodium is obtained without the yellow luminescence: (i) when sodium salts are introduced into a flame of hydrogen in chlorine; (ii) when metallic sodium burns slowly in oxygen, chlorine, or bromine; (iii) when a sodium salt is fused; (iv) when cathode rays act on sodium chloride; (v) when anode rays first act on sodium chloride; (vi) when one heats the coloured residue obtained by the action of anode rays or cathode rays on sodium chloride; and (vii) when sodium chloride is precipitated rapidly from aq. soln. with hydrochloric acid or alcohol. The yellow luminescence of sodium is obtained, accompanied by the fainter blue luminescence: (i) when a sodium salt is introduced into the Bunsen flame; (ii) when sodium burns rapidly in oxygen, chlorine, or bromine; and (iii) when canal rays act on sodium chloride. It is claimed that the yellow luminescence is obtained when sodium vapour is heated; but it is very difficult to be certain that no burning takes place under these conditions.

C. Fredenhagen attributed the yellow luminescence produced by sodium salts in Bunsen's flame to the presence of sodium oxide, and he attributed the absence of the yellow luminescence in the hydrogen-chlorine flame to the absence of sodium oxide. W. D. Bancroft and H. B. Weiser have shown that this hypothesis is probably untenable. E. Wiedemann and G. C. Schmidt attributed the blue luminescence produced by cathode rays to decomposition or recombination: $NaCl \rightleftharpoons Na + Cl$; J. A. Wilkinson showed that the blue luminescence is due to recombination and not dissociation; and this is confirmed by W. D. Bancroft and H. B. Weiser. S. Arrhenius' experiments on the electrolytic condition of the heated vapours of salts led him to assume that when salt is fed into a flame, sodium hydroxide is formed by the action of the steam, and that the hydroxide undergoes ionic dissociation with the production of sodium ions. A. Schuster, P. Lenard, J. Stark, and others have also laid stress upon the part played by ions in flame reactions. W. D. Bancroft and H. B. Weiser add: (i) The yellow luminescence is due to some stage in the process of dissociation; (ii) the diminished intensity of the line spectrum in the hydrogen-chlorine flame, or in the Bunsen's flame fed with a little hydrogen chloride, is due to the forcing back of the dissociation of the alkali salt by the hydrogen chloride; (iii) the absence of the yellow luminescence when sodium burns slowly is due to the small intensity of the light when the reaction is slow; and (iv) since the reacting substance is the electrically neutral vapour of the metal in the case of the line spectrum, there is no migration under electrical stress. Since the reacting substance is the positively charged ion of the metal in

the case of the continuous spectrum, there is a migration to the cathode under electrical stress, as found by P. Lenard.

The spectrum of sodium vapour has been investigated by H. E. Roscoe and A. Schuster.[38] Potassium salts colour the non-luminous gas-flame violet or bluish-violet, and the spectrum contains two characteristic lines: a double line K_α in the extreme red approaching the ultra-red and very near the *A*-line of the solar spectrum—these lines have a wave-length 7697 and 7663 respectively; the other line K_β is near the opposite end of the spectrum in the violet, and it has a wave-length 4044. The emission spectrum of potassium shows many other lines of feebler intensity, thus, H. E. Roscoe and A. Schuster found that the absorption spectra of potassium and sodium show lines in the green, but referred them to the metallic lines of these bodies. G. D. Liveing and J. Dewar showed that the wave-lengths of these lines are 5510 with sodium, and 5730 with potassium, and that they do not coincide with any known metallic lines. W. N. Hartley has compared the spark and the oxy-hydrogen flame spectrum of the alkali metals.

J. N. Lockyer heated a piece of sodium at one end of a vacuum tube, and on sparking he found the vapour arranged itself in layers of different colours. The layer nearest the metal was green, and showed green and red sodium lines without the yellow lines, while the layer above was yellow and showed only the yellow lines. J. N. Lockyer likewise obtained the yellowish-green lines of potassium without the red. He also inquired whether the spectra of an element as it separates out of different combinations containing a different number of atoms of the element in question are identical or not. P. Zeemann found that the spectral lines of sodium are broadened when light from an electric arc is sent through a heated tube containing sodium vapour when placed between the poles of an electro-magnet; and A. A. Michelson showed that "all spectral lines are tripled when the radiations emanate in a magnetic field." W. N. Hartley has investigated the ultra-violet spectrum; H. Becquerel the ultra-red spectrum; E. Wiedemann and G. C. Schmidt the fluorescent spectrum; U. Yoshida studied the effect of an intense electric field on the spectral lines of lithium; S. Datta, the vacuum arc spectra of sodium and potassium.

Rubidium salts impart to the non-luminous gas-flame rather a redder tint than the potassium salts. The emission spectrum of rubidium shows two characteristic lines in the violet Rb_α of wave-length 4202, and the Rb_β of wave-length 4216; there are two others even nearer the extreme red than the red potassium lines named Rb_γ of wave-length 7799; and Rb_δ of wave-length 7950. There are many other feebler rubidium lines. The common spectrum of cæsium has two characteristic blue lines Cs_α of wave-length 4555, and Cs_β of wave-length 4593; there are lines in the red of wave-lengths 6974 and 6722, as well as many other lines. The limits for the recognition of the alkali metals by the visible flame and the visible spark spectra,[39] are, in milligrams:

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Flame spectrum . .	$\frac{1}{600,000}$	$\frac{1}{14,000,000}$	$\frac{1}{3,000}$	$\frac{1}{1,000}$	$\frac{1}{25,000}$
Spark spectrum . .	$\frac{1}{40,000,000}$	—	$\frac{1}{400}$	$\frac{1}{1,000}$	$\frac{1}{4,000}$

E. Mitscherlich[40] and E. Pringsheim showed that no sodium lines are obtained when sodium chloride or hydroxide is heated in a porcelain tube; but that sodium lines are obtained if a reducing agent be present. Hence it was inferred that free sodium is essential for the production of the *D*-spectral line. E. Pringsheim then found that in the cold carbon disulphide flame no *D*-lines are emitted, but they are when the temp. is raised, and he concluded that sodium salts give a yellow light in flames at a lower temp. than when heated in an indifferent atm.; so that the sodium is set free by reduction and not by thermal dissociation. E. Pringsheim heated sodium in a porcelain tube and found the vapour emitted the *D*-lines, but he assumed that this was due to chemical action either with traces of oxygen in

the tube or with the tube itself. *F. Paschen agrees that the glowing of sodium* vapour is not a mere temp. emission. The subject has been further investigated by W. Hittorf and W. Siemens, A. Smithells, J. Evershed, etc. The general conclusion is that heated sodium vapour, like iodine vapour, is probably luminescent. The observed effects are not explained by insisting on thermoluminescence or on chemiluminescence, when sometimes the one and sometimes the other is produced. Although sodium vapour may exhibit thermoluminescence, more or less of any given effect may be due to chemiluminescence. If a substance remains entirely transparent at the highest temp., it will never luminesce or glow. It is generally assumed that the centres of vibration which emit spectral lines are negatively charged corpuscles—electrons; and Zeemann's effect shows that the *D*-lines of sodium are produced by vibrators carrying negative charges. If sodium vapour when heated, breaks up into smaller aggregates or loses electrons, then, as W. D. Bancroft has emphasized, we have chemical reactions in the broader sense of the word, and these may or may not give rise to *light, since it is probable that all reactions* emit light when the reaction velocity is sufficiently high.

R. W. Wood has drawn attention to a deep violet light produced by suspended particles during the condensation of sodium vapour: the colour of the light transmitted through the sodium vapour is deep yellow instead of blue, as usually obtained. It was difficult to understand this at first, since the vapour is perfectly transparent to blue light, and somewhat less so to yellow-green light. The effect was finally traced to a scattering of the violet and *blue rays by the fog of condensing vapour.*

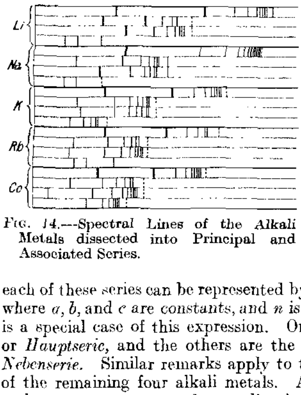

FIG. 14.—Spectral Lines of the Alkali Metals dissected into Principal and Associated Series.

In the search for laws analogous with Balmer's law of the vibration frequencies of the spectral lines of hydrogen, H. Kayser and C. Runge [41] found that the essential property of such spectra is not a simple numerical relation between the vibration frequencies, but rather is the apparently chaotic spectrum of an element resolvable into a number of superimposed regular series of lines. The spectrum of lithium, for example, is compounded of the four series of lines shown in Fig. 14. The lines in each of these series can be represented by a formula of the type $\lambda^{-1}=a+bn^{-2}+cn^{-4}$, where *a*, *b*, and *c* are *constants, and n is an integer; Balmer's formula for hydrogen* is a special case of this expression. One series is regarded as the *principal series*, or *Hauptserie*, and the others are the first, second, and third *associated series* or *Nebenserie.* Similar remarks apply to the component series in the spectra of each of the remaining four alkali metals. All five spectra are such that every line in each spectrum corresponds to a line in each of the other four spectra. Although there is a little doubt about the lithium lines, generally, by increasing the dispersion, the lines can all be resolved into double lines. The dark-red double line in the rubidium spectrum has a corresponding double line in the ultra-red cæsium spectrum; *although G. Kirchhoff and R. Bunsen regarded the blue line as the principal line* of the cæsium spectrum, the energy of the invisible line in the ultra-red exceeds that of all other cæsium lines. Similarly, the double yellow sodium line has an accompanying line in the ultra-violet, and R. W. Wood has photographed forty-eight lines of the series. There is a constant difference in the vibration frequency of the paired lines of the different series of many spectra such that the apparent deviations from constancy lie well within the limits of the errors of observations. With the alkali metals, the difference in vibration frequency between the lines of a pair is proportional to the square of the at. wt. The laws of formation of spectral lines of a group of related elements are dependent upon the at. wt. Thus, in Fig. 14,

as the at. wt. increases the limits of corresponding series move towards the left or red-end of the spectrum, that is, in the direction of slower vibration. This rule may not be applicable to analogous individual lines—*e.g.* the red lithium and the yellow sodium line—because the series contract and therefore shift some lines to the right as the at. wt. increases. In general, in a family group of elements there is a shifting of similar lines towards the less refrangible (red) end of the spectrum as the atomic weights of the elements increase. Thus, the violet pair of lines of potassium is represented by the pair of indigo lines of rubidium, and the two blue lines of cæsium.

In the early days of spectrum analysis, G. G. Stokes and G. Kirchhoff recognized that the absorption of light by a sodium flame, or by sodium vapour, is conditioned by the resonance of the vibrating sodium mol. with that period of the exciting light which was removed; and E. Wiedemann later showed that this absorption is accompanied to some extent by lateral re-emission. R. W. Wood[42] has shown that when sodium vapour is illuminated by a cone of arc- or sun-light, a spot of green fluorescent light appears. The **fluorescent spectrum,** studied by R. W. Wood and J. H. Moore, is made up of an enormous number of fine lines arranged in groups and bands mainly yellow and yellowish-green. If the vapour be exposed to deep violet light, the spectrum suffers no change, but as the wave-length of the light increases, a yellow fluorescence appears and light is emitted of the same wave-length as that absorbed by the vapour. As the wave-length of the incident light is still further increased, the fluorescent light moves along the spectrum in the opposite direction, although in all cases there is an emission of light of the same wave-length as the incident exciting light. Stokes' law is thus violated, particularly when the exciting light is near the middle of the fluorescent spectrum. R. W. Wood also showed that if a bulb containing pure sodium vapour be illuminated by light from a sodium flame, the vapour emits a yellow light without change of wave-length. The emitted light is called the *resonance radiation*, and the corresponding spectrum, the **resonance spectrum.** Attempts have been made by R. W. Wood and co-workers to find if both the *D*-lines appear when sodium vapour is illuminated by a single *D*-line. The results show that the radiation centres in sodium vapour are not entirely independent. If the vessel is perfectly free from hydrogen, and the density of the vapour is low enough, R. W. Wood and L. Dunoyer found that if one of the *D*-lines is used to stimulate the vapour, then that line is alone emitted; but the presence of hydrogen causes both *D*-lines to appear when resonance is excited by one of the *D*-lines; and R. W. Wood and F. L. Mohler add that the transfer of energy from the D_2 to the D_1 emission centres, or *vice versa*, is in some way the result of mol. collisions, either of sodium with hydrogen or sodium with sodium. L. Dunoyer found that polarization can be detected in the *D*-resonance, but R. J. Strutt did not find polarization in the ultra-violet resonance radiation. With dense sodium vapour, R. W. Wood found the *D*-lines are excited when the stimulation occurs in the bluish-green region, and a channelled absorption spectrum is formed; each line of the principal series is also accompanied by a similar channelled spectrum.

According to G. A. Hemsalech,[43] if an alkali chloride, carbonate, or oxide be heated between layers of carborundum, positively electrified particles are emitted—the critical temp. at which the phenomenon occurs varies inversely as the at. wt. of the metal, being 2700° for lithium, and 1900° for cæsium. Of all the elements in the alkali group potassium exhibits the strongest radioactivity. It has not been possible to trace the **radioactivity** of the potassium salts to the presence of minute quantities of any of the known radioactive elements or their active products. N. R. Campbell and R. W. Wood could not detect in the compounds of sodium any radioactivity that was definitely greater than that common to all matter, and certainly no activity $\frac{1}{1000}$th as great as that of potassium. If, therefore, sodium belongs to a radioactive series of elements it must be itself undergoing an immeasurably slow disintegration, or it must be a relatively inactive product of radioactive parent.

F. C. Brown pointed out that if the former is true, sodium left at rest a long period of time should diminish in amount, and if the latter is true, sodium should in time form one or more elements in appreciable quantities. Isolated samples of cæsium salts have been found to exhibit very feeble radioactivity, but cæsium is not yet considered to be radioactive; if the radioactivity should be detectable, the product of its degradation should be an isotope of barium. O. Hahn and M. Rothenbach [44] found the β-activity of rubidium salts of various ages shows no variations such as would be anticipated if the β-rays arose from a relatively short-lived isotope of rubidium, and it cannot be eliminated or affected by chemical purification. The *β-activity of rubidium thus has every characteristic of an atomic property of that element.* The β-rays of rubidium are homogeneous as regards velocity and penetrating power; they are rather more penetrating than the β-rays from uranium; and their velocity is 58 to 60 per cent. of that of light. The β-activity of rubidium is $\frac{1}{15}$th of that due to uranium X for the same weight of uranium; for thorium, the ratio is probably $\frac{1}{10}$th. Applying the law of radioactive change, the product from rubidium should be an isotope of strontium; and from potassium an isotope of calcium. The period of half change of rubidium, calculated from the ratio of its β-activity to that of uranium X_1, is about 10^{11} years, and for potassium probably three times as great. If the age of the oldest felspars is taken as 10^9 years, only 0·17 per cent. of the potassium should have changed into calcium. The period of potassium, however, may be as great as seven times that of rubidium, and it is doubtful if the expected difference of at. wt. would be detectable. E. Rutherford and J. Chadwick obtained evidence of the emission of long-range particles—probably hydrogen—detected by scintillations on a zinc sulphide screen when α-**particles** pass through sodium, but not through potassium. H. R. von Traubenberg found the range of the α-particles in lithium to be $129{\cdot}1\times10^{-4}$ cm. C. W. Hewlett studied the absorption and scattering of homogeneous **X-rays** by lithium.

Chemical properties.—The alkali metals are the most electropositive of the elements; and the electropositive character of the alkali metals is greater, the greater the at. wt., so that cæsium is the most electropositive of all the elements. The alkali metals all tarnish on exposure to air, cæsium fastest of all, and lithium slowest. The oxidation of potassium may proceed so quickly that the heat generated *melts and ignites the metal* which burns with its characteristic violet flame; this is particularly the case when a gentle press. is applied at ordinary temp., the metal then liquefies where the press. is applied, and takes fire—possibly due to the rapid oxidation of the metal at a freshly exposed surface. Analogous remarks apply to rubidium and cæsium, but in a more intense degree, since cæsium normally melts and then takes fire on exposure to the atm. Sodium and lithium do not fire spontaneously in air, and these elements can be heated to their m.p. in air without inflammation. If lithium be heated above 180° it burns brilliantly in air, forming lithium oxide, and more or less of a higher oxide; [45] the products of combustion of each of the other alkali metals in air is a mixture of different oxides. According to P. A. von Bonsdorff, if **air,** or **oxygen** is quite dry, it does not act on the dried metal. Indeed, W. Holt and W. E. Sims distilled sodium and potassium in oxygen which had been thoroughly dried by phosphorus pentoxide; they also found that the flame of the freely burning metal is extinguished by immersion in thoroughly dried oxygen:

> A cylinder into which phosphorus pentoxide has been introduced is inverted over mercury, and left for some days until the moisture has been removed. Freely burning potassium was instantly extinguished in the dry gas, but by raising the deflagrating spoon out of the cylinder the metal re-ignited. The operation can be repeated three or four times before the moist air diffuses into the cylinder sufficiently to support the combustion of the potassium.

If the surface of rubidium or cæsium is quite clean, these two metals inflame spontaneously in thoroughly dried oxygen. G. Reboul found that the presence of

moisture is essential for the *luminescence* which accompanies the oxidation of potassium and sodium.

The alkali metals rapidly decompose **water** at ordinary temp., forming hydrogen and the alkali hydroxide: $2R+2H_2O \rightarrow 2ROH+H_2$. The heat of the reaction $R+H_2O+aq=ROH_{aq}+H$ is between 49·08 and 53·2 Cals. for lithium; 42·4 and 45·0 Cals. for sodium; 41·9 and 48·1 Cals. for potassium; 47·25 and 48·2 for rubidium; and 48·45 and 51·56 Cals. for cæsium.[46] In the case of potassium, rubidium, and cæsium, the heat of the reaction is great enough to ignite the liberated hydrogen, and the flame is tinged by the vapour of the metal. During the reaction, a molten globule of the metal, say, potassium, travels hither and thither on the surface of the water, but is separated from actual contact with the water by a film of steam. The globule becomes smaller and smaller, leaving at last a small bead of fused potash, which bursts explosively when the temp. falls low enough to allow it to come into contact with the water. With sodium, a molten globule also moves about actively on the surface of the water, with potassium the liberated hydrogen ignites spontaneously, with sodium not so, unless the water is warmed over 40°, or the action is localized so that the sodium does not travel about. For instance, the metal ignites if placed on water made viscid by starch paste, or placed on wet filter paper. There is often a much more violent explosion with sodium than with potassium. The cause of the explosion has not been clearly established, although many guesses have been made[47]—*e.g.* the explosion has been attributed to the formation of a hydride, a carbide, or a peroxide; to the inclusion of hydrocarbon oils in the porous metal; etc. Cæsium metal begins to give off hydrogen when in contact with ice at −116°; rubidium at −108°; potassium at −105°; and sodium at −98°. Sodium reacts briskly with **alcohol**, C_2H_5OH, forming sodium ethylate, C_2H_5ONa; according to R. Pictet, the reaction does not take place at temp. below −48°.

The affinity of the alkali metals for hydrogen and the metals is feeble, and for the metalloids, the affinity decreases as the valency of the second element increases. The affinity for the univalent and bivalent elements is usually large. The behaviour of potassium is typical of that of the other members of the family. Lithium salts of all the halides of the alkali metals have the greatest tendency to form hydrated compounds, and the stability of these hydrates is greater, the greater the at. wt. of the combined haloid. Similar remarks apply to the salts of the alkaline earths. **Hydrogen** when heated with the alkali metals forms hydrides. L. Kahlenberg and H. Schlundt[48] studied the occlusion of hydrogen by sodium, and M. Guichard, by potassium. The alkali metals react vigorously with **mercury,** forming amalgams.

Potassium ignites spontaneously in **fluorine** and **chlorine** gases, forming the corresponding halide; but J. A. Wanklyn showed that if the chlorine is dry, the action with sodium is but slight. At −80°, liquid chlorine does not attack the metal. The reaction between potassium, and **bromine** or **iodine** is vigorous, with incandescence. With sodium, the reactions are much less vigorous, fluorine alone attacks the metal at ordinary temp.[49] Bromine attacks the metal but slightly at 200°, and iodine can be fused with sodium in a sealed tube without combination. Sodium is scarcely attacked by **hydrogen fluoride** at ordinary temp.; with dry **hydrogen chloride,** the attack is slight even at the fusion point of the metal—according to J. B. Cohen,[50] a violet or black subchloride is formed. In liquid hydrogen chloride, sodium swells up without giving off gas. With aq. soln. of these acids, the reaction proceeds with explosive violence. Sodium reduces **chlorine peroxide,** ClO_2.

Sulphur and **selenium** unite when warmed with the metal;[51] when sulphur is triturated with sodium, the reaction proceeds with explosive violence which can be moderated by dilution with common salt. Under boiling toluene, sulphur forms the trisulphide Na_2S_3. Selenium forms the monoselenide, Na_2Se, when heated with sodium. Sodium is attacked by **hydrogen sulphide** at ordinary temp., and at the fusion point the metal burns in the gas. Gaseous **ammonia** reacts readily with sodium, and liquid ammonia forms blue soln.—the so-called *alkali-ammoniums*.

Sulphur dioxide is partly absorbed by sodium, and partly reduced to the sulphide; conc. **sulphuric acid** is reduced to the sulphide; the reaction with an acid of sp. gr. 1·84 is less vigorous than with water; but a more dil. aq. soln. of the acid reacts with explosive violence. Boiling **sulphur chloride** does not attack sodium; **thionyl chloride** is completely absorbed by sodium near its m.p. **Nitrogen** does not combine directly with potassium, but lithium unites vigorously with nitrogen below a red heat, and forms the nitride, Li_3N. **Phosphorus, arsenic,** and **antimony** unite directly with the metal. Sodium decomposes **hydrogen phosphide** and **hydrogen arsenide** with the liberation of hydrogen. **Phosphorus trichloride** detonates at the fusion temp. of sodium, and sodium phosphide is formed. **Nitrous oxide** gives sodium oxide between 180° and 200°; the higher nitrogen oxides form mixtures of sodium nitrite and nitrate. Sodium inflames spontaneously in contact with **nitric acid** of a sp. gr. exceeding 1·056. With **meta-phosphoric acid,** some metaphosphate and phosphide are produced. **Boron** does not unite directly with potassium; nor does **silicon** or **carbon. Acetylene** forms carbides K_2C_2 and Na_2C_2; liquid acetylene with sodium forms $NaHC_2$. The alkali metals displace the metals from many oxides and salts—*e.g.* aluminium chloride forms potassium chloride and aluminium. When heated with an alkali metal, **silicon fluoride** forms silicon, hydrogen, etc.; **boron fluoride** forms boron. With mercury oxide and sodium, $HgNa_2O_2$ is formed. The alkali metals also reduce many oxides—*e.g.* with **boric oxide,** boron is formed: $B_2O_3+6K=2B+3K_2O$, and the potassium oxide unites with the excess of boric acid, forming a borate. Liquid **carbon dioxide** is scarcely attacked; but at a red heat, free carbon, sodium oxide, and carbonate are formed; **carbon monoxide** under the same conditions gives similar products; **carbon disulphide** is attacked in the cold. Sodium attacks many minerals which are insoluble in acids—*e.g.* **silicates, tungstates, titanates, molybdates, chromite,** and **cassiterite. Silica, glass,** and **porcelain** are also attacked by the alkali metals. Potassium is not so soluble as sodium in the fused **hydroxides;** thus, 8 to 9 grms. of the metal potassium dissolve in 100 grms. of fused potassium hydroxide at 480°, and from 0·5 to 1·3 grms. at 700°; while 25·3 grms. of sodium dissolve in 100 grms. of sodium hydroxide at 480° and 6·9 at 800°. Equilibrium in each case is attained very slowly. G. von Hevesy [52] found the solubility of sodium in fused sodium hydroxide to be

	480°	600°	610°	670°	760°	800°
Na	25·3	10·1	9·9	9·5	7·9	6·9

expressed in grms. per 100 grms. of the fused alkali hydroxide. Similarly, with potassium in fused potassium hydroxide, he found at 480°, 7·8–8·9 grms. of potassium; at 600°, 4–3; at 650°, 2–2·7; and at 700°, 0·5–1·3. The solubility of sodium is lowered by the presence of thallium, cadmium, and gold, but no definite result was observed with the alkali halides.

Uses of the alkali metals.—Up to about 1890, the main, perhaps the only, use of the metal sodium was in the manufacture of aluminium. When the electrolytic process for aluminium was established, it appeared as if the production of sodium on a large scale would cease; but an application of the electrolytic process for sodium so cheapened this element that it could be employed in processes where previously its high cost had prevented its use. For example, large amounts of sodium are now converted into sodium peroxide used in bleaching, etc.; also into alkali cyanides used in gold extraction, in electroplating, photography, etc. Sodium is used in the aniline dye industry and in making organic compounds when a powerful reducing agent is needed—*e.g.* artificial indigo. Sodium amalgam was formerly used in the extraction of gold from crushed quartose rock; and the amalgam, like the metal, is an important reducing agent. An alloy of potassium and sodium, liquid at ordinary temp., is used for some high temp. thermometers above the b.p. of mercury.

The atomic weights of the alkali metals.—A. Arfvedson, the discoverer of

lithium, made an attempt in 1817 to determine the at. wt. of this element. He assumed that the oxide has the composition LiO_2; to-day, the oxide is taken to be Li_2O, so that, assuming Arfvedson's determination was correct, his value would be four times that now accepted. In 1826, however, J. J. Berzelius reasoned that this element forms no sesquioxide, and, from the analogy with the other elements which form no sesquioxides, he preferred the formula LiO. In his celebrated table of at. wt., 1826, J. J. Berzelius represented the three alkali oxides then known by the general formula RO. However, as a result of the work of C. F. Gerhardt, J. J. Berzelius' formula for the alkali oxides RO was changed to R_2O, and Berzelius' at. wt. were accordingly halved. In 1849, H. V. Regnault determined the sp. ht. of the alkali chlorides, and from the analogy with other related chlorides, he assigned to the alkali chlorides the formula R_2Cl_2, and to the oxide, R_2O; this was confirmed in 1862, when H. V. Regnault found the at. ht. of, say, lithium to be 6·6 in agreement with Dulong and Petit's rule, provided the at. wt. of lithium be 7; this made the formula for the oxide Li_2O. For similar reasons, H. V. Regnault maintained that the oxides of sodium and potassium should be represented by the formulæ Na_2O and K_2O respectively. J. J. Berzelius advocated the formulæ LiO, NaO, and KO to the day of his death, 1848—probably because he assigned a far greater weight to evidence based on chemical rather than on physical grounds. The formulæ Li_2O, K_2O, and Na_2O are those accepted to-day, and they are in harmony with the isomorphism of the more complex compounds of lithium and sodium and of the alkali metals generally; although lithium itself often behaves differently from the other elements of the family group. The grouping of lithium with the alkali metals is also confirmed by Mendeléeff's classification; from the fact that in aq. soln. of its salts lithium, like the other four metals in the alkali family, behaves as a univalent cation. The univalency of the members of the alkali family of metals is further in agreement with the vapour density determinations of the metals and the volatile salts; and with the mol. wt. of soln. of different salts in various solvents.

Comparatively few at. wt. have been fixed by direct comparison with hydrogen or oxygen; most of them have been determined by reference to silver, chlorine, bromine, iodine, potassium, sodium, nitrogen, carbon, or sulphur as an intermediary, which in turn is referred to the oxygen or hydrogen standard. By international agreement, oxygen is the primary standard, and therefore these elements are to be regarded as intermediate or secondary standards, which are essentially bound up with the at. wt. of the other elements. The accurate determination of these intermediate or secondary standards is therefore of great significance. Determinations of the at. wt. of potassium and sodium were made by J. J. Berzelius, T. J. Pelouze, and J. C. G. de Marignac. This gave a relation between potassium or sodium and the halogen. In one group of determinations, the mol. wt. of the alkali halide was obtained by the decomposition of a known weight of a chlorate, bromate, or iodate; and in a second group of determinations, silver chloride, bromide, or iodide was precipitated from a soln. of alkali halide. The silver was the connecting link between the at. wt. of the halogen and the alkali metal.

EXAMPLE.—Careful measurements show that 100 grms. of potassium chlorate, $KClO_3$, furnish 60·846 grms. of potassium chloride, KCl. Hence, if the at. wt. of oxygen be 16, it follows that 48 grms. of oxygen in potassium chlorate correspond with 74·593 grms. of potassium chloride. Again, 100 grms. of silver dissolved in nitric acid are required for the precipitation of the chlorine in 69·1138 grms. of potassium chloride, and 130·9478 grms. of silver chloride are obtained. Hence, 74·593 grms. of potassium chloride require the eq. of 107·928 grms. of silver for precipitation, and furnish 143·329 grms. of silver chloride and contain 107·928 grms. of silver and 35·401 grms. of chlorine, and consequently also 74·593 grms. of potassium chloride contain 35·401 grms. of chlorine, and 39·190 grms. of potassium. Hence, the at. wt. of silver, chlorine, and potassium are respectively 107·9, 35·4, and 39·19, when the at. wt. of oxygen is 16.

As a result of various determinations[53] of the at. wt. of *potassium* ranging from J. J. Berzelius' 39·26 in 1811 to T. W. Richards and E. Müller's 39·114 in

1907, the best representative value is taken to be **39·15** (oxygen 16). Similarly, numbers ranging from J. J. Berzelius' 23·105 in 1826 to T. W. Richards and R. C. Well's value 23·008 in 1905 have been recorded for the at. wt. of sodium;[54] the best representative value is taken to be **23·05** (oxygen 16). The early determinations of the at. wt. of *lithium* were made on impure samples, probably contaminated with sodium;[55] and accordingly, the numbers are rather high, ranging from 7·65 to 10·7. The later numbers range from R. Hermann's 6·1 in 1829 to T. W. Richards and H. H. Willard's 6·939 in 1910. The best representative value of all reliable determinations is taken to be **7·03** (oxygen 16). The values[56] for *rubidium* range from R. Bunsen's 85·36 in 1861 to Archibald's 85·483 in 1904. The best representative value is taken to be **85·4** (oxygen 16). The at. wt. of *cæsium* ranges[57] from R. Bunsen's value 132·661 in 1861 to T. W. Richards and E. H. Archibald's 132·879 in 1903. The best representative value is taken to be 132·9 (oxygen 16). The numbers for lithium were determined by the analysis of the sulphate, carbonate, chloride, and the perchlorate; the numbers for rubidium by the analysis of the chloride, bromide, and sulphate; and for cæsium by the analysis of the chloride, bromide, and nitrate. There are several indications of a missing element in the alkali series with a higher at. wt. than cæsium. In Mendeléeff's periodic table there is a gap corresponding with *eka-cæsium;* and the at. numbers also show a corresponding gap as indicated by H. G. J. Moseley, M. Siegbahn and E. Friman, etc. T. W. Richards and E. H. Archibald, L. M. Dennis and R. W. G. Wyckoff, and G. P. Baxter[58] fractionally crystallized pure cæsium nitrate, derived from specimens of pollucite, etc., while in search of the unknown alkali metal. The at. wt. of the different fractions were virtually the same, and the flame spectra of the different fractions showed no line not present in all that were examined.

The relative density of potassium vapour at 1040° (H unity) is between 40 and 45; very nearly corresponding with monoatomic molecules.[59] The vapour densities of the alkali metals are somewhat inaccurate because they attack the containing vessels. The value for sodium, between 15·1 and 25·8, also agrees with a monatomic mol. W. Ramsay's experiments on the effect of potassium on the f.p. of mercury show that the alkali metals are possibly univalent in mercurial soln. C. T. Heycock obtained similar results from the effects of lithium, and potassium on the f.p. of sodium; and of sodium on the f.p. of cadmium, tin, lead, and bismuth.

F. W. Aston[60] has shown that the positive ray spectrum of lithium shows the existence of two **isotopes** of at. wt. 6 and 7; sodium shows no isotope; potassium shows two isotopes with at. wt. 39 and 41; rubidium shows two isotopes of at. wt. 85 and 87; and cæsium has possibly two isotopes.

Analytical reactions of the salts of the alkali metals.—The salts of the alkali metals are not precipitated from aq. soln. by dil. hydrochloric acid; hydrogen sulphide, alkali or ammonium sulphide, ammonium carbonate or phosphate (excepting with lithium), barium or calcium hydroxides. A soln. of lithium or sodium salts does not readily give a precipitate with *hydrochloroplatinic acid* or *tartaric acid*, because the corresponding salts are readily soluble in water; with soln. of potassium salts not too dil., hydrochloroplatinic acid gives a yellow precipitate and tartaric acid a white precipitate. The former acid precipitates rubidium and cæsium salts even more readily than potassium salts, because the rubidium salt, and still more the cæsium salt, are less soluble than potassium chloroplatinate. The rubidium tartrate is more soluble than potassium tartrate and the cæsium salt is more soluble still, so that precipitates with tartaric acid are produced only in conc. soln. *Hydrochlorostannic acid*, H_2SnCl_6, produces a white precipitate with cæsium salts, and with rubidium salts in very conc. soln.; potassium, sodium, and lithium salts give no precipitate with this acid. A soln. of *antimony trichloride* in hydrochloric acid acts similarly. *Sodium phosphate*, Na_2HPO_4, produces a precipitate only with lithium salts in soln. of moderate conc.; the reaction is

quantitative only in soln. made alkaline with caustic soda, evaporated to dryness, and washed with ammonia water. *Ammonium carbonate*, $(NH_4)_2CO_3$, in ammoniacal soln. precipitates lithium carbonate from moderately conc. soln. of lithium salts in the absence of considerable amounts of the other alkali chlorides or of ammonium chloride. The other alkali salts give no precipitate under the same conditions. *Ammonium fluoride* soln. in excess precipitates lithium salts alone from moderately conc. soln. of lithium salts. Ammonia favours the precipitation. *Sodium cobaltinitrite—Koninck's reagent*—prepared by acidifying a soln. of 5 parts crystalline cobalt nitrate, 10 parts of sodium nitrite, and 100 c.c. of water with a few drops of acetic acid—gives a yellow precipitate with potassium salts, but not with salts of sodium, lithium, rubidium, cæsium, magnesium, the alkaline earths, zinc, aluminium, etc. A yellow coloration produced is sensitive to nearly 1 : 50,000. Ammonium salts should be absent, since they too give a precipitate sensitive to 1 : 20,000, and almost rivalling in delicacy Nessler's test. *Silico-molybdic acid* gives an insoluble precipitate of cæsium silico-molybdate, and a slightly soluble precipitate of rubidium silico-molybdate, and still more soluble precipitates of the other alkali salts. *Perchloric acid* produces a precipitate with potassium, rubidium, and cæsium salts. *Bismuth-sodium thiosulphate—Carnot's reagent*—prepared by adding a few drops of sodium thiosulphate to a drop of dil. bismuth nitrate and adding 10–15 c.c. of absolute alcohol, and if the soln. is turbid, adding water until the turbidity just clears—gives a yellow precipitate of bismuth potassium thiosulphate with potassium but not with sodium salts. Ammonium chloride inhibits the reaction. *Hydrofluosilicic acid* in excess gives a gelatinous precipitate with soln. of potassium rubidium, and cæsium salts. *Potassium pyroantimoniate*, $K_2H_2Sb_2O_7$, gives a white precipitate in neutral or feebly alkaline, not acid, soln. of sodium salts. Many salts of the metals give analogous precipitates with this reagent. A filtered soln. of potassium dihydroxytartrate, $K_2(C_4H_4O_8)H_2O$, dissolved in the least possible quantity of water, gives a sparingly soluble precipitate with sodium salts; by using ice-cold soln., H. J. H. Fenton[61] detected one part of sodium in 2000 parts of water by its means. Cæsium carbonate is alone soluble in absolute alcohol, the carbonates of the other four alkalies are but very sparingly soluble. Lithium chloride is alone soluble in a mixture of absolute alcohol and ether, the chlorides of the other four alkalies are but sparingly soluble. If rubidium chloride, containing a little cæsium and potassium chlorides, be dissolved in conc. hydrochloric acid and be treated with a soln. of *antimonious chloride* in the same acid, all the cæsium with a little rubidium will be precipitated as a mixture of $3CsCl.2SbCl_3$, or $Cs_3Sb_2Cl_9$, and $3RbCl.2SbCl_3$, or $Rb_3Sb_2Cl_9$. The filtrate, after concentration, can be treated with hydrogen sulphide to remove the antimony, and the filtrate evaporated, taken up with conc. hydrochloric acid, and treated with an excess of *stannic chloride*. The rubidium is precipitated almost quantitatively as Rb_2SnCl_6, while the potassium remains in soln. as K_2SnCl_6. Wash the precipitated Rb_2SnCl_6 by decantation with conc. hydrochloric acid, dissolve it in water, and remove the tin by hydrogen sulphide. Fairly pure rubidium chloride can be obtained from the filtrate. *Alum* produces a precipitate in soln. of cæsium salts of moderate conc., and in conc. soln. of rubidium salts under conditions where no precipitation occurs with salts of the other alkalies. A *non-luminous gas flame* is coloured reddish-violet by cæsium, rubidium, and potassium salts; sodium salts give a yellow flame which makes a stick of red sealing-wax appear yellow, whereas a luminous gas-flame makes the sealing-wax appear orange. Lithium salts colour the flame carmine red. Sodium salts may mask the colour produced by the other salts, but not if the flame is viewed through blue cobalt glass. The spectroscope is a delicate indicator of the absence or presence of these salts in the flame reactions. In quantitative analysis, the mixed chlorides of potassium and sodium are weighed and the alcoholic soln. is treated with hydrochloroplatinic acid, or perchloric acid. The precipitated potassium salt is weighed, and the corresponding amount of potassium chloride is calculated. The sodium chloride is then estimated by difference. If lithium chloride be present it is first

washed out with a soln. of amyl alcohol and ether. The rubidium and cæsium chlorides are precipitated with the potassium salt.

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§ 8. The Binary Alloys of the Alkali Metals

Purity is not always a desideratum with the metals since pure metals often possess undesirable qualities from an industrial point of view. Copper is one of the few metals which in its pure state has an important field of usefulness, since it is a far better conductor of electricity than the less pure metal. Gold and silver used in jewellery, etc., are alloyed with other metals, chiefly copper, in order to give them hardness and durability without destroying their appearance. Alloys possess the same general physical characters as the elementary metals, but they are mixtures, solid soln. or mixed crystals, or chemical compounds—*e.g.* the brasses are alloys of copper and zinc, the steels are alloys of iron and carbon, etc. The solubility curve of one metal in another can usually be represented by a curve quite analogous to the solubility curve of a salt in water. The soln. during cooling may congeal to a homogeneous solid, or some of the components may separate from the soln., and a polished and etched surface of the cold metal may show its heterogeneous character when examined by oblique reflected light under the microscope. New alloys of the metals are being constantly investigated, since the properties of a metal or alloy may be modified in an extraordinary manner by the addition of another metal. The subject is of great importance in the industries.[1]

It is sometimes very difficult to prove whether two metals unite with one another to form chemical compounds, because the isolation of crystals from reguline matters by the action of a solvent is only possible when the one is more resistant than the other. As previously indicated, the existence of maxima on the equilibrium curve is valid evidence which is applicable only to the conditions under which the curve was obtained. If liquid oxygen and hydrogen were mixed together and an equilibrium curve obtained, if no other evidence were available, it might be inferred that these two elements do not unite chemically. The data with alloys have usually been obtained at high temp., and it is probable that many compounds are not stable under these conditions; but the methods of investigation have been extended by the prolonged annealing of the alloys at temp. below their fusing points—*e.g.* lead and antimony are said to form a compound Pb_2Sb_3 at a temp. of 245°, nearly 4° below the eutectic temp. Similar remarks apply to several other binary mixtures —*e.g.* tin with lead, bismuth, nickel, zinc, cadmium, or mercury. The evidence is mainly based on arrests in the cooling curve of these alloys. Many physical properties are profoundly modified by the formulæ of definite compounds, so that when the relations between the variations of a physical property with the composition are examined, a discontinuity in the corresponding curve may depend upon the appearance of a new phase, or it may mark the limit of the saturation of a solid soln. Unlike the density or sp. vol., the electrical and thermal conductivities vary continuously within the limits of miscibility of two metals if the number of molecules increases or decreases continuously from one limit to the other. If a definite compound is formed in solid soln. with both its components, the corresponding curve may show a singular point where the conc. of the compound is a maximum.[2]

G. Tammann, in his papers *Ueber die Fahigkeit der Elemente miteinander Verbindungen zu bilden*,[3] has reviewed the results of investigations on a great number of binary mixtures of the metallic elements, and he infers:

(1) *Neighbouring elements belonging to the same natural group do not usually form compounds with one another.* For example, binary compounds of the members of the following four groups are not known: (i) copper, silver, gold; (ii) zinc, cadmium, mercury; (iii) germanium, tin, lead; (iv) arsenic, antimony, bismuth. In the groups: iron, nickel, cobalt, no compound of cobalt with iron or nickel is known, but nickel and iron form the compound Ni_2Fe. Iodine, bromine, and chlorine are exceptions in forming binary compounds with one another.

(2) *A given element forms compounds with all the members of the same natural group or with none.* Thus, copper forms no compound with thallium or bismuth;

similar remarks apply to silver and gold. Copper forms compounds with zinc, cadmium, aluminium, tin, and antimony, and compounds of all these three elements with silver and gold are known. Copper and tin form a series of compounds, but *no compound of copper and lead is known. Zinc and cadmium form no compounds* with bismuth, lead, and aluminium, but they do react with antimony and sodium. Zinc and cadmium do not unite with tin, but a compound of tin and mercury is known. The rule does not hold good when there is a change from the non-metallic to the metallic character in a group of elements, as is exemplified by the difference in the combining capacity of antimony and bismuth for other elements. The rule does not apply to the first two short periods in Mendeléeff's table—*e.g.* magnesium forms compounds with zinc, cadmium, and mercury; sodium unites with potassium, etc. Lead and tin form no compounds with antimony or bismuth. Bismuth forms no compounds with aluminium, gold, or silver, but antimony does form compounds with each of these elements—*e.g.* AlSb, ZnSb, Zn_3Sb_2, $AuSb_2$, $SbAg_3$. Copper and silver form no binary compounds with lead, but gold and lead form two compounds. Neither zinc nor cadmium forms a binary compound with thallium, while mercury does form a compound. Aluminium combines with zinc but not with cadmium; manganese and copper each unites with tin, but not with lead. Aluminium unites with metals of the iron group, but thallium does not. Platinum and palladium each gives a compound with lead, but nickel does not. Allowing for exceptions of this kind, the members of a group of elements thus appear to be related somewhat like the members of a homologous series of carbon compounds.

Among over a hundred binary compounds of the metals examined, relatively few agree with the valencies of the elements as exhibited in their salts—*e.g.* the valencies of the elements in $NaZn_{12}$, $NaCd_5$, $NaHg_4$, $FeZn_7$, $NiZn_7$, $AuSb_2$, $NiCd_5$, etc., do not agree with their ordinary values, although the higher compounds of iodine with the metals approximate with these binary metal compounds. The valency of antimony in its compounds with the metals corresponds most closely with the valency which that element exhibits in its salts. This is probably connected with the fact that among the elements considered, antimony is most closely related with the metalloids. The formulæ of the compounds which a metal forms with the members of a natural group are not always analogous, and this in spite of the many chemical analogies between the members of that group. The compounds of aluminium with copper and silver—$AlCu_3$, $AlAg_3$—and with silver and gold—$AlAg_2$, $AlAu_2$—are analogous, so also are analogies exhibited by the compounds of tin with copper and silver—Cu_4Sn, Ag_4Sn—and with copper and gold—CuSn, AuSn. Similar analogies are exhibited by

Cu_3Sb	Mg_2Sn	Mg_3Sb_2	Zn_3Sb_2	ZnSb	$SbTl_3$
Ag_3Sb	Mg_2Pb	Mg_3Bi_2	Cd_3Sb_2	ZnSb	$BiTl_3$

On the other hand, the binary compounds of sodium with zinc, cadmium, and mercury, or with tin and lead, have no such analogies with one another. The sodium compounds of bismuth and antimony are analogous, but the characteristics of these latter elements approximate to those of the metalloids.

The formation of binary compounds is obviously conditioned by the chemical affinity of the elements concerned, and, borrowing an old analogy, R. Abegg (1906) suggested that the union is determined by the polarity of electro-affinity of the elements, and this acts like the attraction of positive and negative charges of electricity. The greater the polar difference of the components, the greater the tendency to chemical union, and the greater the stability of the resulting product. Elements with a marked difference in polarity are designated *heteropolar*, and elements with a closely related polarity are called *homopolar*. Heteropolar elements usually stand some distance apart in the periodic table, and they are exemplified by the union of such compounds as KCl, Al_2O_3, HgS; while homopolar elements form compounds like the metal alloys and amalgams, and compounds of the metalloids with one another—*e.g.* ICl. Two elements in the same natural group do not

generally form compounds because these elements are homopolar, and such compounds usually have a feeble electro-affinity—aluminium unites with boron, but not with the higher members of the same family; similarly, silicon unites with carbon, but not with the higher members of the same family. The greater the heteropolarity of a pair of elements, the more likely are they to combine in accord with their normal valency, and homopolar pairs under similar conditions are more likely to combine in varying proportions differing from their normal valency. The phosphides of the strongly electropositive elements like the metals of the alkalies or alkaline earths have marked heteropolar characteristics, while the phosphides of the weakly electropositive elements like iron and copper have marked homopolar characteristics.

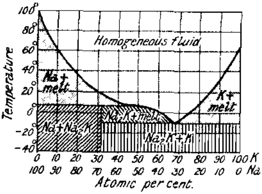

FIG. 15.—Equilibrium Curves of Alloys of Potassium and Sodium.

A few of the relations of the alkali metals with one another have been investigated. Potassium with about 30 per cent. of sodium forms an alloy which is liquid at ordinary temp., and which has the appearance of mercury. This becomes pasty at 8°, and solidifies at a lower temp. If the alloy contains 77 per cent. of potassium, it remains liquid even below 0°. The alloys are most conveniently prepared by melting together the two metals under rock oil. In some cases sodium displaces potassium from its combinations—*e.g.* according to J. A. Wanklyn, when sodium is added to fused potassium acetate, gases are rapidly evolved, but the reaction is not completed; an alloy of the two metals is formed. G. Williams [4] obtained an alloy of the two metals with 76·5 per cent. sodium by treating potassium hydroxide under a hydrocarbon oil with sodium at a temp. not exceeding 171°. The alloy can be converted into a peroxide, and it has been used under the name *pneumatogen* for the revivification of vitiated air in life-saving apparatus.

According to E. B. Hagen, the alloy with a composition corresponding with NaK melts at 4·5°; and, according to M. Rosenfeldt, the alloy with equal weights of the two metals melts at 6°. A. Joannis (1887) inferred the existence of a compound NaK_2 from his observations on the heats of formation of the alloys of potassium and sodium. In opposition to this, N. S. Kurnakoff and N. A. Puschin found that the mixture corresponding with K_2Na represented a eutectic point at −12·5° in the f.p. curve of a mixture of the two elements when about 66 atomic per cent. of potassium is present. G. van Bleiswyk obtained the f.p. curve indicated in Fig. 15, and this shows that the compound Na_2K is the only one formed under these conditions, and it is liable to dissociation into sodium and liquid at about 6°. No solid soln. is formed. There is a large gap in the f.p. curve of both lithium-sodium and lithium-potassium alloys, as indicated for sodium-lithium alloys in Fig. 16. According to G. Massing and G. Tammann,[5] the gap represents an immiscible mixture, for the alloy separates into two liquids within the proportions indicated. The addition of 6·3 per cent. of sodium to lithium lowers the f.p. from 179° to 162°, and further additions do not affect the f.p. until about 97 per cent. of sodium has been added when further additions lower the f.p. rapidly down to that of sodium itself, viz. 97°. The dotted line, *ab*, Fig. 16, represents the solubility of sodium in lithium, and *cd* the solubility of lithium in sodium; the solubilities of these elements in one another probably increase as the temp. rises, and finally a critical temp. is obtained above which the two elements are miscible in one

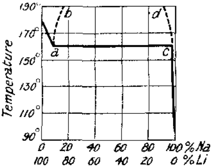

FIG. 16.—Equilibrium Curve of Alloys of Lithium and Sodium.

another in all proportions. Lithium and potassium behave similarly, the flat terrace in the curve appears at 166° and extends through the series from 7 per cent. of potassium to 97 per cent. The metals potassium, rubidium, and cæsium appear to have little tendency to form alloys with one another. The electrical conductivity curve of solid alloys of potassium and rubidium at 25° has a flat minimum, and the curves for liquid alloys between 50° and 150° has no minimum. The temp. coeff. of the electrical conductivity gave a curve which is nearly flat, but which has no minimum. The hardness curve has a marked maximum near the potassium end of the series.[6] J. W. Hornbeck found that the temp. coeff. of the thermal conductivity rises with rise of temp. Alloys of lithium with sodium, or cæsium, or rubidium have not been studied. Lithium is much more prone to form alloys with the metals than is cæsium, rubidium, potassium, or sodium, and in this respect, lithium resembles magnesium.

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§ 9. The Hydrides of the Alkali Metals

J. L. Gay Lussac and L. J. Thénard [1] referred to the absorption of hydrogen by potassium at a red heat, and stated that a grey powder with no metallic lustre was formed which did not melt at a red heat, and which was decomposed by contact with mercury into hydrogen and potassium amalgam; similarly, by contact with water. In the latter case, one quarter as much again hydrogen is obtained as the contained potassium can furnish on contact with water. The work of J. L. Gay Lussac and L. J. Thénard would make potassium hydride, K_4H. In 1808, like J. Dalton, these two investigators seem also to have suggested that potassium itself "may be a compound of hydrogen and potash," but H. Davy demonstrated that this assumption would not explain the facts.

In 1874, P. Hautefeuille and L. Troost [2] found that lithium, sodium, and potassium absorb hydrogen without changing their metallic appearance, much as does palladium. These metals can be melted in hydrogen without absorbing the gas; with potassium and sodium, absorption begins at about 200°, and attains a maximum between 300° and 400°. Potassium absorbs 124·6, and sodium 238, times its volume of gas under a press. of 760 mm. According to H. Moissan, potassium between 200° and 400° absorbs 126 vols. of hydrogen, and sodium between 300° and 421°, 237 vols. C. Matignon says that lithium absorbs no hydrogen; but, at 500°, absorbs 17 times its volume of gas under the same conditions. P. Hautefeuille and L. Troost assumed that compounds Na_2H and K_2H were formed; and they measured the dissociation press. of the supposed compounds at different temp.:

	330°	350°	370°	390°	400°	410°	420°	430°
K_2H . . .	45	72	122	363	548	736	916	1100 mm.
Na_2H . .	28	57	100	284	447	598	752	910 mm.

The product in each case is a crystalline, brittle, silver-white mass with a metallic lustre.

If lithium, in an iron boat in a hard glass tube, be heated to redness in a stream of hydrogen, the metal burns with incandescence, forming a hard mass of lithium hydride. A. Guntz obtained a similar product by heating lithium nitride in a stream of hydrogen; and a mixture of lithium hydride and carbide, by heating lithium in a stream of acetylene. Lithium hydride so prepared is a hard white mass which melts at 680°, at which temp. its dissociation press. is 27 mm. The empirical composition corresponds with the formula LiH. H. Moissan prepared potassium and sodium hydrides by heating the metals to about 360° in a similar manner. A tangled mass of snow-white crystals of the hydride sublimed on the cooler side of the tube. According to A. Holt, when sodium is heated in an atm. of hydrogen at about 270°, the surface is dulled owing to the formation of a thin film of hydride which protects the metal from rapid attack; if the temp. be raised to 400°, the sodium remains bright and the hydride sublimes on to the cooler parts. The hydride is formed at 380°, but it remains dissolved in the metal. Thus, L. Troost and P. Hautefeuille found that the hydrogen absorbed by a given amount of sodium at 380° corresponds with the formula Na_2H. Hence, as the temp. of sodium heated in hydrogen gas at atm. press. rises about 270°, more and more of the hydride is dissolved by the metal; the ratio Na : NaH decreases; and the vap. press. of the hydride increases until at length, in the vicinity of 380°, the hydride begins to sublime. At this temp., the composition of the solid corresponds with L. Troost and P. Hautefeuille's Na_2H or Na : NaH. The formation of this easily dissociating compound or soln. of constant composition is quite consistent with the sublimation of the hydride NaH. Cæsium and rubidium hydrides were similarly prepared by keeping the temp. below 300°. If the hydride contains an excess of the metal, it can be purified by washing it with liquid ammonia; the alkali metal dissolves, the hydride remains.

K. Moers says that lithium hydride crystallizes in the cubic system; and he gives 0·8196 for the **specific gravity** of lithium hydride at about 20°. Sodium hydride has a sp. gr. 0·959 when sodium itself has a sp. gr. 0·970. The **molecular heat** is 0·34 at −199°; 0·67 at −180°; and 4·09 at 19·7°. P. Günther also measured the mol. ht. of lithium hydride. The value of $\beta\nu$ is 825. According to J. Moutier, the **heat of formation** of the sodium-hydrogen product at 330° is 13 Cals. and of the potassium derivative, 9·3 Cals. per gram of hydrogen; these magnitudes increase with rise of temp. and attain a maximum value between 390° and 400°—afterwards the heats of formation decrease with rise of temp. It is not clear from P. Hautefeuille and L. Troost's record whether they were dealing with a solid soln. of hydrogen and the metal, or with a chemical compound. The valency of the elements in these supposed hydrides, K_2H and Na_2H, also seems peculiar, for the alkali metals seem here to be semi-valent. A. Guntz, and K. Moers found the heat of formation of lithium hydride to be $(Li, \frac{1}{2}H_2) = 21·6 \pm 0·250$ Cals.

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Sp. gr. . . .	0·816	0·92	0·80	2·0	2·7
Heat of formation .	21·6	16·60	—	—	— Cals.

The hydrides do not conduct electricity, and they cannot be compared with the alloys of hydrogen and the metals; but according to K. Moers, the **electrical conductivity** at 443° is $2·124\times10^{-5}$; at 597°, $3·225\times10^{-3}$; at 692°, 0·04049; and at 754°, 1·01; or the electrical conductivity, k, at $\theta°$, between 500° and 754° is $0·265\times10^{-4}+1·8\times10^{-7}(\theta-500)^2+1·95\times10^{-11}(\theta-500)^4+0·5\times10^{-21}(\theta-500)^8$. J. Elster and H. Geitel found that the hydrides of sodium, potassium, rubidium, and cæsium are coloured by exposure to **cathode rays.** E. F. Seiler studied the **photoelectric effect** *with the hydrides of sodium, potassium, rubidium, and* cæsium.

In 1840, V. A. Jaquelain founded a method of separating hydrogen from its admixture with methane and ethylene on the absorption of hydrogen by potassium; and G. Gehlhoff used the absorption of hydrogen by the alkali metals in order to obtain the pure gas. The alkali hydrides decompose readily in moist air, and tumultuously in **water**. Hydrogen is liberated but without incandescence; *e.g.* $LiH+H_2O=LiOH+H_2+31\cdot6$ Cals. Analyses of these hydrides are in accord with the formulæ LiH, NaH, KH, RbH, and CsH, and no other hydrides have been observed.

Neither potassium nor sodium hydride dissolves in carbon tetrachloride, turpentine, ether, or benzene; but both are soluble in the molten metals. The latter resembles the products obtained by P. Hautefeuille and L. Troost, which were therefore solid soln. of the hydride in the metal. When heated in vacuo, a little below red-heat, the hydrides decompose into the metal and hydrogen, and the metal sublimes. O. Ruff gives for the decomposition of sodium hydride a temp. over 330°, and for potassium hydride a temp. over 200°.

W. Nernst has suggested that the hydrogen in lithium hydride plays the part of a halogen, and likens the reaction $LiOH+H_2=H_2O+LiH$ with $LiOH+HCl=H_2O+LiCl$; he shows similarities between lithium hydride and chloride in their crystalline form, at. vol., at. ht., heat of formation, coloration of ultra-violet rays, etc. The electrolysis of molten lithium hydride is also analogous with that of fused lithium chloride. Since lithium hydride is completely hydrolyzed in aq. soln., it is assumed that hydrogen acts as a very weak acid.

The chemical activity of the alkali hydrides is greater, the greater the at. wt. of the basic element. Potassium hydride burns spontaneously in **fluorine** and **chlorine,** forming halides of the metal and some hydrogen halide. Sodium hydride is slowly attacked by dry gaseous chlorine but not by liquid chlorine at −35°, nor does it react with **bromine** in the cold, or at the b.p. of the halogen; but it does react with incandescence with **iodine** at 100°. Lithium hydride is not attacked by cold chlorine, but it does so when heated. Potassium hydride also unites in the cold with **oxygen** and air; sodium hydride inflames at 230° in oxygen; but is not attacked by liquid oxygen; lithium hydride has no action in the cold, but combustion occurs when the compound is heated. Potassium hydride decomposes **hydrogen chloride:** $HCl+KH=KCl+H_2$; at a gentle heat, it forms potassium formate with moist **carbon dioxide:** $CO_2+KH=H.COOK$, and some free carbon; with dry carbon dioxide, carbon and the alkali carbonate are formed; and it reacts with **acetylene** at 100°, forming $C_2K_2.C_2H_2$ and hydrogen [3]: $2C_2H_2+2KH=C_2H_2.C_2K_2+2H_2$, though there is nothing to show why both sides of the equation should not be divided by two. Rubidium, cæsium, and sodium hydrides react similarly; the latter with difficulty. With thoroughly dried acetylene no reaction occurs below 42°, but if moisture be present, the reaction is vigorous even at −60°. There is no reaction at 100° with the hydride and methane, or with ethylene. Potassium hydride forms potassium hyposulphite with **sulphur dioxide:** $2SO_2+2KH=K_2S_2O_4+H_2$, at low temp.; and a mixture of sulphate and sulphide at higher temp. Sodium hydride reacts vigorously with **sulphur** vapour, but not with **hydrogen sulphide;** the alkali hydrides are decomposed when gently heated with hydrogen sulphide, and also with many metal oxides. Conc. **sulphuric acid** forms sulphur and hydrogen sulphide; it is also vigorously attacked by **hydrochloric and nitric acids. Carbon disulphide** reacts with cæsium hydride, but not with sodium or potassium hydride at ordinary temp. When cæsium hydride is heated with **nitrogen,** a cæsiumamide is formed; lithium hydride forms lithium nitride; **phosphorus** acts on cæsium hydride like nitrogen does, and when the products are treated with water, ammonia is obtained in the one case, phosphine in the other. Liquid **ammonia** has no action, but when heated with gaseous ammonia, the alkali amides are formed. **Arsenic** acts on the hydride only at an elevated temp., nor does **carbon, boron,** or **silicon** act at temp. below the decomposition point of the hydride. K. Moers represented the reaction with **mercury** by

$LiH+Hg=LiHg+\frac{1}{2}H_2$. The hydrides are strong reducing agents—the **oxides of lead, copper,** etc., are reduced to the metallic state. Lithium hydride slowly decomposes absolute **alcohol,** forming the alcoholate and hydrogen; the hydrated alcohol is vigorously decomposed. The alkali hydrides are insoluble in **ether** and **benzene.**

If hydrogen is passed over heated potassium, the rising gas spontaneously inflames in air, and forms a cloud which has alkaline properties; if the gas be cooled, it loses its spontaneous inflammability. L. Sementini [4] obtained a spontaneously inflammable gas in preparing potassium by the action of iron on potassium hydroxide at a high temp. He called this gas a term eq to *kaliuretted hydrogen*. According to J. J. Berzelius and C. Brunner, it deposits finely divided potassium on cooling. The so-called kaliuretted hydrogen is probably a mixture of finely divided potassium or potassium hydride, KH, and hydrogen, and not a gaseous potassium hydride.

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§ 10. The Oxides of the Alkali Metals

Three years after the discovery of the alkali metals, and eight years before L. J. Thénard discovered *l'eau oxygénée*, the products of their oxidation were investigated by J. L. Gay Lussac and L. J. Thénard, and by H. Davy. It now seems remarkable that J. L. Gay Lussac and L. J. Thénard did not discover hydrogen peroxide by the action of water on the oxidation products of the alkali metals, but they assumed that water acts on these oxides giving soda or potash with the evolution of oxygen. Only small quantities of the metals were used in the experiments and the oxidation proceeded at the high temp. produced when the metals were burned. Both sets of investigations failed to establish the nature of the alkali oxides.

The three metals cæsium, rubidium, and potassium are oxidized in the cold in moderately well-dried air. Cæsium inflames immediately on contact with air or oxygen. A part of the oxide is volatilized as a yellow sublimate, and the brown or yellow mass which remains, gives off oxygen on contact with water. This shows that a peroxide has been formed. The spontaneous ignition of cæsium makes its manipulation difficult; rubidium, also, is very liable to spontaneous inflammation in air; but potassium rarely inflames on exposure to air. Sodium inflames only at an elevated temp., and it forms the two oxides, Na_2O and Na_2O_2. Lithium is not attacked at ordinary temp. in dry air or in dry oxygen; but it combines with incandescence with oxygen above 200°, forming the monoxide, Li_2O, and a trace of the dioxide, Li_2O_2. Potassium and sodium can be distilled in thoroughly dried oxygen without oxidation. E. Rengade [1] could not dry oxygen well enough to prevent the spontaneous inflammation of cæsium, but, below −80°, the action is

almost insensible, although the surface of the metal shows signs of oxidation after a few minutes' exposure.

If the press. of the oxygen is less than 1 cm. of mercury the metal melts and assumes a brown colour without losing its metallic lustre; it then changes to a reddish-brown colour, and the temp. gradually rises. A film then begins to develop about the edges of the metal; this film partly dissolves but ultimately covers the whole surface with a black crust and the absorption of oxygen then ceases. When this solid is heated, it melts to a brown liquid, which absorbs oxygen, and again becomes solid. It is therefore assumed that four oxides of cæsium are here in evidence.

The authentic oxides of the five alkali metals are:

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Monoxides	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
Dioxides	Li_2O_2	Na_2O_2	K_2O_2	Rb_2O_2	Cs_2O_2
Trioxides	—	(Na_2O_3)	(K_2O_3)	—	(Cs_2O_3)
Tetroxides	—	—	K_2O_4	Rb_2O_4	Cs_2O_4

The sesquioxides may be solid soln. or mixtures of two other oxides—say, R_2O_2 and R_2O_4.

The alkali monoxides.—H. Davy [2] believed that he had prepared the monoxides of potassium and sodium by treating the hydroxides with the metal; "there is," he said, "a division of the oxygen between the alkali and the metal," the oxides were also made by heating the metals in a stream of oxygen; but, according to N. N. Beketoff, the monoxides are not formed under these conditions, and he claims that Davy's reaction: $KOH+K=K_2O+H$, is reversible, and the product is impure.

H. Davy, and J. L. Gay Lussac and L. J. Thénard in their early work on sodium and potassium, observed that each peroxide is transformed into the corresponding monoxide at a high temp. The product, however, is still contaminated with the peroxide. The same oxide is obtained in an impure form by calcining the nitrate or nitrite [3] in the absence of air—*e.g.* $5K+KNO_3=3K_2O+N$; and $6K+2KNO_2=4K_2O+N_2$; the impure oxide is also formed by heating metallic sodium with nitrate or nitrite, or with barium nitrite or nitrate, or with manganese dioxide.[4]

A. V. Harcourt [5] showed that the monoxide is not obtained by calcining the peroxide in a silver dish, but rather a mixture of the monoxide with silver oxide or possibly a compound, $KAgO_2$. N. N. Beketoff claimed [6] to have made rubidium monoxide by heating the metal in air and subsequently reducing the mixture of oxides so formed by heating it with the metal in an atm. of nitrogen. H. Erdmann and P. Köthner (1897) believed that rubidium monoxide did not exist. W. Holt and W. E. Sims [7] have also shown that the oxide formed by heating potassium in the theoretical amount of dry air always contains the metal, and presumably also some higher oxide.

J. J. Berzelius stated [8] that potassium monoxide, which he called *Wasserfreies Kali*, can be obtained only by the combustion of the metal in the right amount of oxygen necessary for the formation of the oxide; if the metal be heated in a limited supply of air which does not contain enough oxygen for the formation of the *Wasserfreies Kali*, Berzelius also said that a grey **potassium suboxide** is formed corresponding with the formula K_4O—present notation. He says the same suboxide is formed by heating one part of the metal with 1·2 parts of the hydroxide to a temp. not exceeding 300°. S. Lupton [9] tried to verify this observation, but he failed to confirm the existence of the suboxide since his product was merely a mixture of the metal and the hydroxide. W. Holt and W. E. Sims also failed. The product is either a solid soln. of the metal and the oxide, or else a mixture of the two. Similar remarks apply to the suboxide of sodium, Na_4O, and probably also to R. de Forcrand's suboxide,[10] Na_3O, which he claims to have formed by heating sodium a little over its m.p. in air free from carbon dioxide. It appears as a grey porous surface crust, which on exposure to air gradually becomes white by further oxidation. It reacts violently with water, giving off hydrogen. Heat of soln. 97·78 Cals.; heat of formation, Na_3O, 38·8 Cals. E. Rengade [11] found that the fusion curve of soln. of cæsium monoxide

in cæsium metal showed maxima corresponding with the existence of four **cæsium suboxides**, viz. Cs_7O, Cs_4O, Cs_7O_2, and Cs_3O. These formulæ do not accord with the univalency of cæsium.

In making the oxides of the alkali metals by the direct action of oxygen, the temp. rises so high that the containing vessel is attacked, and the oxygen must accordingly be diluted with an inert gas, or rarefied in order to lessen the violence of the reaction. Gmelin recommended burning the metal in nitrous oxide, N_2O, nitric oxide, NO, or nitrogen peroxide, NO_2, and he claimed the product was then the alkali monoxide. W. Holt and W. E. Sims, however, found that with nitrous oxide, potassium and sodium furnished, not the monoxide, but an oxide or mixture of oxides approximating RO or R_2O_2; and that if nitric oxide or nitrogen peroxide be employed, a mixture of varying proportions of the nitrite and nitrate are formed, but not the oxide. When lithium is directly oxidized by an excess of oxygen, lithium monoxide, Li_2O, and a trace of lithium peroxide is formed; with sodium, the dioxide, Na_2O_2, is produced; and with potassium, rubidium, and cæsium, the oxides RO_2 and R_2O_4 result.

It is very difficult to prepare the monoxides by the action of oxygen on the heated metals because the product is really a mixture of the unconverted metal and of the monoxide along with one or more of the higher oxides. E. Rengade,[12] however, in his *Contribution à l'étude des oxydes anhydres des metaux alcalins* (1907), has shown that the monoxides of potassium, sodium, rubidium, and cæsium may be prepared by oxidizing the alkali metals with less than the theoretical amount of oxygen. The oxygen is admitted very slowly and the press. kept below 2 cm. of mercury so as to avoid a rise of temp. which would result in the formation of higher oxides. The monoxide dissolves in the excess of metal which is then distilled off in vacuo. The residual oxide remains in the form of small crystals.

L. Troost [13] prepared lithium monoxide by burning the metal in an iron boat in a stream of dry oxygen. The product is contaminated with a little peroxide which imparts a yellow tinge to the metal; L. Troost made the same oxide by heating a mixture of lithium carbonate and carbon to a high temp.; and also by heating lithium nitrate for a long time in a silver crucible. W. Dittmar made this oxide by heating the carbonate in a stream of hydrogen for about 36 hrs. at a red heat; and by heating the hydroxide to a red heat.

The properties of the alkali monoxides.—The monoxides of the alkali metals have the following properties:

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Colour	White	White	White	Golden-yellow	Orange red
Sp. gr. (0°)	1·80	2·25	2·31	3·72	4·36
Heat of formation	141·2	89·96	92·08	94·90	99·98 Cals.
Heat of hydration	31·20	56·50	75·00	80·00	83·2 „

The heats of formation correspond with the reaction: $2K+O=K_2O$; and the heats of soln. with $K_2O_{solid}+H_2O_{liquid}=2KOH_{solid}$, all the oxides with water give the alkali hydroxide, but no hydrogen. They are soluble in alcohol.[14]

Orange-red cæsium monoxide changes to carmine-red, and purple as the temp. is raised; it appears black at 150°. The colour changes are reversed on cooling. At the temp. of liquid oxygen, −180°, the colour becomes pale yellow. Cæsium monoxide is volatile in vacuo at about 250°, and it melts with decomposition between 360° and 400°; it then forms the dioxide and the vapour of the metal: $2Cs_2O=Cs_2O_2+2Cs$. This reaction shows that the monoxide is rather unstable and has a tendency to decompose into a mixture of the metal and a higher oxide. The yellow colour of rubidium monoxide also becomes deeper in tone with a rise of temp.; at 200° it has a golden colour. Rubidium monoxide breaks down into the dioxide and rubidium vapour at 400°. Cæsium monoxide can dissolve or absorb the vapour of the metal, and the monoxide dissolves in the molten metal. Cæsium monoxide commences to absorb **hydrogen** at 150°, forming the hydride; the

reaction: $Cs_2O+H_2=CsOH+CsH$, is rapid at 170°–180°, and no metal is sublimed. According to N. N. Beketoff,[15] sodium monoxide is formed by heating sodium with the hydroxide, but the monoxide is decomposed by hydrogen, so that the reaction: $2Na_2O+H_2\rightleftharpoons 2NaOH+2Na$, is reversible. Cæsium monoxide is completely reduced by hydrogen at ordinary temp. According to E. Rengade,[16] **fluorine** has no appreciable action on cæsium monoxide in the cold, but when heated to 150° or 200°, the mass becomes incandescent, and a blue flame appears; **chlorine** and **iodine** act in a similar way. **Oxygen** scarcely affects the monoxide in the cold, but at 150°, absorption begins, and the peroxide, Cs_2O_4, is formed. Molten **sulphur** in vacuo reacts vigorously, forming a sulphide or polysulphide and a sulphate: $4Cs_2O+4S=Cs_2SO_4+3CsS$. Heated with **phosphorus,** a phosphide and phosphate are formed. Neither amorphous **boron** nor sugar **charcoal** reacts below the temp. at which the monoxide is decomposed. Hydrogen sulphide forms a hydrosulphide with incandescence at ordinary temp. **Sulphur dioxide** bleaches the oxide at ordinary temp.; and when heated, the reaction is attended by incandescence, and when the resulting white mass is dissolved in water a sulphide and a sulphate are formed. Liquid **ammonia** acquires a fugitive blue colour and forms a white residue of cæsium amide: $Cs_2O+NH_3=CsNH_2+CsOH$; it is thought that the fugitive blue coloration is evidence of an intermediate reaction: $2Cs_2O+2NH_3=Cs_2O_2+2CsNH_3$, and the products then break down: $Cs_2O_2+2CsNH_3=2CsOH+2CsNH_2$. Moist **carbon dioxide** attacks cæsium oxide with inflammation at ordinary temp., and the dry gas acts at about 250° or 300°. Incandescence also occurs in the presence of **carbon monoxide.** With sodium monoxide, carbon dioxide forms the carbonate at 400°; with carbon monoxide at 290°–310°, the reaction $2Na_2O+CO=Na_2CO_3+2Na$ occurs; and at 320° a black compound of carbon monoxide and sodium begins to be formed.[17] The chemical properties of rubidium monoxide closely resemble those of the cæsium compound. Potassium monoxide with *dil.* hydrocyanic acid [18] evolves 60 Cals. per mol., K_2O; hydrosulphuric acid gives 154 Cals.; carbonic acid, 220 Cals.; and boric acid (B_2O_3), 200 Cals. According to P. Lebeau,[19] *lithium monoxide forms isomorphous mixtures with* **lime.** *According to L. Troost, and to W. Dittmar, lithium monoxide does not attack* **platinum** *at a white heat if air be excluded.*

The higher alkali oxides.—*J. L. Gay Lussac and L. J. Thénard's* [20] *measurements* of the amount of oxygen which united with a given weight of potassium burning in oxygen showed that "potassium combines with twice or even three times as much oxide as it requires to pass into the state of potash," *i.e.* potassium monoxide; they further showed that "no volatile product is formed during the oxidation," since "the weight of the oxide obtained is always equal to that of the potassium employed and of the oxygen absorbed." With respect to the oxidation of sodium, also, it was found that "the metal can take up half as much oxygen again as it requires to pass into the state of sodium monoxide, or even more;" while with potassium, the weight of oxide formed agrees with the supposition that the body is a trioxide, K_2O_3. J. L. Gay Lussac and L. J. Thénard, however, did not regard their experiments as decisive, and while confirming this work, H. Davy stated that he did not find "any means of ascertaining accurately the quantity of oxygen contained in these new oxides." C. F. Schönbein also prepared these oxides by the combustion of the metals in air or oxygen; he called these oxides *antozonides*, and accordingly inferred that they should not give off oxygen in contact with water. He ascribed the evolution of oxygen which actually occurs to the rise of temp., and found that if the water is kept cold "a liquid is obtained which decolorizes potassium permanganate soln. . . .," and attributed the observed results to the presence of hydrogen peroxide in the soln.

A. V. Harcourt [21] found that while the tetroxide, K_2O_4, is the end-product of the oxidation of potassium, the dioxide, Na_2O_2, is the end-product of the oxidation of sodium. A. V. Harcourt was unable to prepare an intermediate oxide, K_2O_3, of definite composition. He noticed that the oxidation occurs in two stages when

a mixture of nitrogen with gradually increasing amount of oxygen is admitted to molten potassium at about 100°. He says :

The grey film covering the metal changes to a deep blue, the surface appears to become roughened by little wrinkles and projections, and a moment arrives when a single spluttering spark appears at one point, and a dust of white oxide rises. At this instant, the absorption of oxygen begins . . . the blue crust becomes white. Immediately afterwards it disappears entirely beneath the surface of the liquid metal, whose smooth surface is soon broken by innumerable projections which ascend and ramify with a steady, visible growth, having the white lustre of frosted silver. At the same time the metal climbs rapidly up the surface of the glass . . . by capillary attraction through the bulky powder and extends in broad foliations, which grow together from side to side, and sometimes cover the whole interior of the bulb. Gradually, as the oxidation proceeds, the inner surface of the bulb changes to a dead white, and the brilliant undergrowth crumbles down to a shapeless powder. . . . Before all the dark metal foliations have quite disappeared some portions of the oxide begin to acquire a yellow colour, and the yellow colour gradually spreads throughout the mass as the press. of the oxygen is increased. The white oxide is potassium dioxide ; the yellow oxide, potassium tetroxide. The phenomena with sodium at about 200° are far less striking, and the metal does not spread itself on the glass. Only the dioxide is formed.

S. Lupton showed that the dioxide, K_2O_2, is formed by the continued action of dry air or oxygen on potassium, and he described the complex oxides, K_8O_5, K_6O_4, K_4O_3, as *mixtures or aggregates of the di- and mono-oxide*—K_2O_2 and K_2O—in varying proportions, but he did not show how the mono- or di-oxide could be obtained. W. Holt and W. E. Sims prepared the di-, tri-, and tetra-oxides of potassium—K_2O_2, K_2O_3, and K_2O_4. A. Joannis also obtained the same three compounds by the oxidation of potassammonium under different conditions ; and he also made sodium di- and tri- oxide by the oxidation of sodammonium with oxygen.

N. N. Beketoff[22] prepared rubidium mono- and tetra-oxide in 1889 ; H. Erdmann and P. Köthner considered that the tetroxide of rubidium is the only definite rubidium oxide whose existence has been demonstrated, but E. Rengade (1907) succeeded in preparing all four oxides, Rb_2O, Rb_2O_2, Rb_2O_3, and Rb_2O_4. E. Rengade also made the corresponding four cæsium oxides. There is little to show that the so-called trioxides are not mixtures of the di- and tetra-oxides.

L. J. Thénard (1827) did not prepare lithium peroxide ; he merely "assumed, by analogy with baryta, soda, and potash, that heating lithium in oxygen would furnish the peroxide." Traces of lithium dioxide, Li_2O_2, mixed with much monoxide were obtained by L. Troost,[23] in 1856, by burning the metal in oxygen ; and the pure compound was prepared by R. de Forcrand, in 1900, by the action of hydrogen on an aq. soln. of lithia. The resulting crystals have the composition of trihydrated **lithium dioxide dihydroperoxide**, $Li_2O_2.H_2O_2.3H_2O$, and when left about 8 days in vacuo over phosphorus pentoxide, the anhydrous dioxide Li_2O_2 remains. In general, the tendency of the alkali metals to peroxidation is greater the greater the at. wt. of the element.

The alkali dioxides or peroxides.—*As just indicated, lithium forms only traces* of the dioxide, Li_2O_2, when heated in oxygen, and the dioxide has to be prepared indirectly by treating lithium hydroxide with hydrogen peroxide, and drying the product in vacuo over a desiccating agent. The combustion of sodium in an excess of dried air or oxygen furnishes sodium dioxide. The metal is contained in glass, aluminium, silver, or platinum vessels which are rather more attacked than when potassium is employed. H. Y. Castner[24] used an aluminium vessel, and a stream of air in which the proportion of oxygen was gradually increased. The peroxide containing about 93 per cent. Na_2O_2, is made on a manufacturing scale by placing sodium on aluminium trays supported on carriages continuously travelling through a tunnel kiln heated to about 300°, and through which a stream of air—freed from moisture and carbon dioxide—also passes. The trays are charged at one end of the kiln, and emptied at the opposite end.

Sodium dioxide is obtained in an impure form, but suitable for many industrial purposes by heating to redness a mixture of lime or magnesia with sodium nitrate in a stream of air or oxygen. H. C. Bolton made the peroxide by adding small pieces of sodium to a mixture of sodium nitrate and sodium hydroxide heated to nearly its m.p. The reddish-brown liquid loses its colour on cooling. The nitrate is reduced to ammonia by the sodium : $NaNO_3+3NaOH+2Na=3Na_2O_2+NH_3$. B. C. Brodie also made the peroxide by heating a sodium salt with barium peroxide.[25] If molten sodium hydroxide be exposed to oxygen, under press., some sodium peroxide is formed.

The formation of potassium dioxide by direct oxidation has been previously indicated. W. Holt and W. E. Sims [26] made a substance with the same composition as potassium dioxide, K_2O_2, by heating the metal in a quantity of nitrous oxide insufficient for complete oxidation. A. Joannis obtained this same oxide as a rose-coloured gelatinous precipitate, by passing a slow current of oxygen through a soln. of potassium in liquid ammonia cooled to $-50°$; the current is continued until the soln. is decolorized. E. Rengade [27] made cæsium dioxide, Cs_2O_2, by gradually allowing the theoretical amount of oxygen to enter an evacuated glass vessel holding an aluminium boat containing a known weight of cæsium metal. The temp. was rapidly raised. The fused mass attacks glass, nickel, silver, platinum, etc. Aluminium is the most resistant of all the metals tried.

Sodium dioxide is an important commercial product ; the other alkali peroxides are more of the character of chemical curiosities. According to J. Scott,[28] sodium dioxide has a micro-crystalline structure. Some of the properties of the dioxide are tabulated in the following scheme :

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Colour	White	White	White	Yellowish-white	Pale yellow
Sp. gr.	—	—	—	3·72 (0°)	4·47 (15°)
Heat of formation, R_2O_2 .	144·8	119·8	—	—	— Cals.

The heats of transformation of the monoxides to the dioxides increases regularly with increasing at. wt. The dioxides are soluble in water. Sodium dioxide dissolves in water without decomposition if a rise of temp. be prevented.[29] The heat of soln. of lithium dioxide, Li_2O_2, is 7·19 Cals. at 20° ; and of sodium dioxide, Na_2O_2, 14·41 Cals. If only a small quantity of water is used, the dioxide decomposes into the hydroxide and oxygen. Some hydrates have been prepared. For instance, A. V. Harcourt [30] prepared **octohydrated sodium dioxide,** $Na_2O_2.8H_2O$, by concentrating an aq. soln. of the dioxide, but, according to R. de Forcrand, it is best prepared by cooling, at 0°, a soln. of the dioxide in four times its weight of water. G. F. Jaubert made it by exposing sodium dioxide for about two weeks to an atm. sat. with water vapour, but free from carbon dioxide. T. Fairley made the hydrate by the action of hydrogen peroxide on an aq. soln. of the hydroxide in excess, and evaporation in vacuo, and the precipitation of the hydrate by the addition of alcohol to the aq. soln. The hydrate furnishes large tabular crystals of hexagonal form. The heat of formation: $Na_2O_2+8H_2O=Na_2O_2.8H_2O+34·08$ Cals. The hydrate is scarcely altered by keeping it for a week at a winter's temp. ; it melts at 30° in its own water of crystallization, with a brisk evolution of oxygen. According to A. V. Harcourt, if the octohydrate is allowed to stand over conc. sulphuric acid, it continues to lose water for about nine days ; the weighings then become constant. The composition approximated with **sodium dioxide dihydrate,** $Na_2O_2.2H_2O$. The hydrate forms **sodium percarbonate,** $Na_2CO_4.8H_2O$, when treated with solid or liquid carbon dioxide, and with an excess of carbon dioxide the **acid sodium percarbonate,** $4Na_2CO_4.H_2CO_3$.

According to E. Schöne, if a soln. of one eq. of sodium hydroxide with 3·5 to 4 eq. of hydrogen peroxide be evaporated in vacuo—preferably in darkness—small colourless crystals are formed, with a composition approximating to tetrahydrated **sodium dioxide dihydroperoxide,** $Na_2O_2.2H_2O_2.4H_2O$. The crystals soon become opaque. They are very soluble in water, sparingly soluble in alcohol. The compound begins to decompose at 62°, with the evolution of oxygen. The crystals gradually decompose on keeping. If sodium dioxide be suspended in carbon tetrachloride and treated with hydrogen chloride, a colourless

compound—**sodium dioxide dihydrochloride**, $Na_2O_2.2HCl$—is formed. This decomposes when treated with water, forming a mixed soln. of hydrogen peroxide and sodium chloride. Other mol. compounds have been prepared by G. F. Jaubert—$Na_2O_2.2H.COOH$; $Na_2O_2.2C_6H_5COOH$, etc. For the corresponding trihydrated **lithium dioxide hydroperoxide**, $Li_2O_2.H_2O_2.3H_2O$, *vide supra*.

Sodium peroxide is a white powder which becomes darker and darker when heated, and as in the analogous phenomena with the oxides of zinc and tin, the white colour is restored on cooling. Sodium peroxide can be heated to its m.p. without decomposition. It is hydrated by exposure to moist air free from carbon dioxide, but, in the presence of the latter gas, sodium carbonate is formed. Sodium peroxide is an energetic oxidizing agent, and the aq. soln. behaves as if it were an alkaline soln. of hydrogen peroxide (*q.v.*). Fused sodium peroxide attacks most metals—tin, silver, platinum, etc. C. Zenghelis and S. Horsch [31] found that the reaction with carbon dioxide: $CO_2+Na_2O_2=Na_2CO_3+O+55,225$ cals., is more vigorous than with carbon monoxide: $CO+Na_2O_2=Na_2CO_3+123,330$ cals., in spite of the greater thermal value of the latter reaction. It is believed that endothermic percarbonate is first formed with carbon dioxide, $Na_2C_2O_6$, and that this at once decomposes $Na_2C_2O_6=Na_2CO_3+CO_2+O$. When a current of carbon dioxide is passed over a mixture of sodium dioxide with a readily oxidizable substance, including aluminium and magnesium, the reaction occurs explosively with iron the metal forms Na_2FeO_4 without explosion; with zinc and copper a preliminary heating is required. A mixture of powdered aluminium and sodium dioxide explodes when heated to redness, or exposed to humid air. The silicates and many native oxides which are not readily attacked by fused sodium carbonate are decomposed by fused sodium peroxide. Hence, it is sometimes used for decomposing these substances prior to analysis. The fusion is usually conducted in nickel crucibles—gold and silver have been used. Platinum is rapidly attacked by the fused oxide, while the other metals just mentioned are not attacked so quickly. Sodium dioxide does not explode by collision, by shock, or by heating; but, when mixed with oxidizable substances, explosive mixtures may be formed. Many carbon compounds are rapidly oxidized by sodium dioxide. A mixture of calcium carbide and sodium peroxide is explosive.

Commercial sodium dioxide contains about 90 to 92 per cent. of the dioxide, or 19 to 20 per cent. of active oxygen. The powder usually has a yellow tint owing to impurities—sodium hydroxide, and carbonate, alumina, and traces of iron. The latter is bad, since it makes the peroxide liable to catalytic decomposition when moist. Sodium dioxide is the active agent in several commercial products. A mixture with a neutral salt—say, magnesium chloride or sulphate—is used for bleaching,[32] disinfection, and other oxidizing purposes. The powdered product is very sensitive to air, and accordingly G. F. Jaubert [33] proposes to compress it into cubes; D. E. Parker fuses and casts it into briquettes or cubes, when its trade name is *oxone;* oxone is used for making oxygen. A compressed mixture of sodium dioxide and chloride of lime is G. F. Jaubert's *oxolith*, also used for making oxygen. Various other mixtures are sold for bleaching and other purposes under various trade names.

There is the same difficulty about the constitutional formulæ for the alkali peroxides or dioxides as occurs with hydrogen peroxide; and it is convenient to regard these compounds as derivatives or salts of hydrogen peroxide, H_2O_2, which is regarded as a dibasic acid. In sodium dioxide both hydrogen atoms are displaced by sodium, but J. Tafel [34] has prepared derivatives with only one hydrogen atom displaced from the mol., viz. NaO_2H or NaO.OH, *sodyl* or *natryl hydroxide;* or **sodium hydrogen peroxide,** and constituted, according to J. Tafel, Na—O—OH,

HO	NaO	NaO
HO	HO	NaO
Hydrogen peroxide.	Sodium hydrogen peroxide.	Sodium peroxide.

Sodium hydrogen dioxide remains as a white powder on shaking pulverulent sodium dioxide with an ice-cold mixture of alcohol and conc. hydrochloric, nitric,

or sulphuric acid; or with absolute alcohol alone: $Na_2O_2+C_2H_5OH=NaO_2H+C_2H_5ONa$, if an acid be also present, the sodium alcoholate forms alcohol and a salt of the corresponding acid. Sodium hydrogen peroxide is soluble in water at 0° and has a smaller heat of soln. than sodium dioxide. The aq. soln. is strongly alkaline, and when warmed, decomposes into sodium hydroxide and oxygen; if the dry salt is warmed, it is liable to decompose explosively. According to H. T. Calvert's measurements of the electrical conductivities of soln. of sodium hydroxide and hydrogen peroxide, a relatively large proportion of sodium peroxide, in aq. soln., is hydrolyzed. If an excess of hydrogen peroxide be present, the hydrolysis can be restricted. He demonstrated the presence of anions O_2'; and of the anions O_2'' in soln. where the hydrogen peroxide is in excess and in a strongly alkaline soln. of hydrogen peroxide, the ions are Na· and O_2''.

Sodium hydrogen peroxide decomposes slowly at ordinary temp. When treated with dil. alcohol, $Na_2O_2.8H_2O$ is formed; if the aq. soln. be neutralized with hydrochloric acid, chlorine is evolved on heating; and with sulphuric acid, at ordinary temp., a liquid is obtained which reduces potassium permanganate with the evolutions of oxygen. Alcoholic hydrochloric acid at −5° furnishes a compound containing $NaCl.NaO_2H$, at higher temp. sodium chloride and hydrogen peroxide are formed. With acetic acid, in alcoholic soln., $2CH_3COONa.H_2O_2$, is formed. Aq. soln. of this salt are neutral. Sodium hydrogen peroxide is converted into sodium carbonate, water, and oxygen by the action of dry carbon dioxide and an unstable percarbonate is formed by the action of the same gas on the aq. soln. at low temp.[35] When sodium hydrogen peroxide is treated with absolute alcohol or hydrogen peroxide the product $2NaO_2H.H_2O_2$ is formed,[36] and the same substance is obtained by the action of sodium alcoholate (ethoxide), C_2H_5ONa, on a mixture of 30 per cent. hydrogen peroxide with absolute alcohol; and also by the action of an ethereal soln. of anhydrous—100 per cent.—hydrogen peroxide on metallic sodium. F. Horton measured the electrical conductivity of the solid oxide.

The trioxides of the alkali metals.—According to E. Rengade, rubidium or cæsium trioxide is formed as a chocolate brown or black mass by gradually introducing the theoretical amount of oxygen into an evacuated vessel containing the metal in an aluminium boat; and afterwards raising the temp. to the fusion point of the mixture. Rubidium trioxide fuses at about 470°, and cæsium trioxide at about 400°; the former has a sp. gr. 3·53 (0°), and the latter 4·25 (0°). These oxides are decomposed by treatment with water, forming hydrogen peroxide, oxygen, and the alkali hydroxide. E. Rengade[37] says that rubidium trioxide, and hence also cæsium trioxide, is not likely to be a mixture of the di- and tetra-oxides because it appears as a black mass during the progressive oxidation of the metal, after the formation of the yellowish-white rubidium dioxide, and before the yellow tetroxide appears. W. Holt and W. E. Sims obtained potassium trioxide as a pale reddish-yellow solid by heating potassium in an excess of nitrous oxide; and R. de Forcrand, by heating the tetroxide in vacuo at 480°. A. Joannis obtained potassium trioxide by stopping the action of a slow current of oxygen on a soln. of potassammonium in liquid ammonia at −50°, at the moment when the brick-red precipitate has the deepest colour; by the prolonged action of oxygen on a soln. of sodammonium in liquid ammonia at −50°, A. Joannis likewise obtained a rose-coloured precipitate, of sodium trioxide, Na_2O_3. If the current of oxygen is rapid, the precipitate, at the moment the soln. is decolorized, has the composition $NH_3.Na_2O$, or $NH_2.Na_2OH$. In aq. soln., sodium trioxide furnishes oxygen gas and A. V. Harcourt's octohydrated dioxide. According to R. de Forcrand, the heats of formation of the four alkali trioxides starting from their elements are sensibly the same, and equal to 126 Cals.

The tetroxides of the alkali metals.—The highest oxide formed by lithium is the dioxide, and with sodium the trioxide; potassium, rubidium, and cæsium form tetroxides. A. V. Harcourt[38] showed that the indications of the higher oxides of potassium observed by J. L. Gay Lussac and L. J. Thénard, and by H. Davy, about 1810, probably represented the formation of potassium tetroxide. The

methods used for the preparation of sodium dioxide furnish potassium tetroxide if applied to potassium. A. V. Harcourt heated the metal to about 180° in an atm. of nitrogen, and gradually displaced this gas by air or oxygen. All traces of moisture were rigorously excluded. Potassium, rubidium, and cæsium tetroxides are the ultimate products of the oxidation of the corresponding metals in an excess of oxygen or air. The metal is best contained in an aluminium boat during the reaction; the product fused; and was allowed to cool in oxygen at ordinary press.

H. C. Bolton made potassium tetroxide by melting potassium with potassium nitrate; E. de Haen by heating a mixture of potassium nitrate with lime or magnesia, and afterwards in a current of air or oxygen between 300° and 500°; and A. Joannis obtained it as a chrome-yellow precipitate by the prolonged action of oxygen on a soln. of potassammonium in ammonia at −50°. The orange-yellow product obtained by A. von Baeyer and V. Villiger by the action of ozone on dry potassium hydroxide is probably potassium tetroxide.

The tetroxide of potassium is often called potassium peroxide, while sodium peroxide is the dioxide. The potassium compound is orange-yellow, the rubidium and cæsium compounds are yellow with a faint red tinge. The **specific gravities** of rubidium and cæsium tetroxides are respectively 3·05 and 3·68 (0°); and the respective **melting points** are approximately 280°, 600°, and about 515° in an atm. of oxygen. Rubidium tetroxide gives off oxygen readily at about 500°, and if kept at 550° in a vessel in communication with the mercury pump, it forms the black trioxide; cæsium tetroxide loses oxygen at about 350°. The **heat of formation** [39] of potassium tetroxide from its elements is 133·74 Cals.; of rubidium tetroxide, 137·6 Cals.; and cæsium tetroxide, 141·46 Cals.; the heats of formation of the tetroxides from their monoxides are respectively 46·94, 54·1, and 58·76 Cals. The tetroxides absorb moisture from the air, and on deliquescing give off bubbles of oxygen. They dissolve rapidly in **water,** forming hydrogen peroxide with the evolution of oxygen in accord with the equation: $Cs_2O_4+2H_2O=2CsOH+O_2+H_2O_2$. Cæsium tetroxide is not attacked by absolute **alcohol,** but, when heated, the oxide gradually dissolves with the evolution of oxygen. The tetroxides are reduced by **hydrogen** at about 300° with the formation of the alkali hydroxide, water, and oxygen. H. Erdmann and P. Köthner explained this curious reaction by assuming a preliminary formation of hydrogen peroxide. V. Meyer (1897) [40] considers this hypothesis doubtful because, dry silver oxide, potassium peroxide, etc., also furnish oxygen when warmed in a stream of hydrogen, carbon monoxide, or carbon dioxide. Here the formation of hydrogen peroxide is excluded, and the reactions with potassium peroxide are explained: $K_2O_4+CO=K_2CO_3+O_2$; $2K_2O_4+2CO_2=2K_2CO_3+3O_2$; and $K_2O_4+H_2=2KOH+O_2$. **Carbon,** and carbonaceous compounds react vigorously with the tetroxides when heated, forming the alkali carbonates. **Carbon monoxide** reacts with the tetroxide at a temp. rather more than 100°, forming the same volume of oxygen as of carbon monoxide consumed in the production of the carbonate: $K_2O_4+CO=K_2CO_3+O_2$. "The perfect constancy in the volume of the gas throughout the experiment," said A. V. Harcourt (1861), "goes also to prove that the two actions proceed proportionally, the carbonic oxide is substituted for an eq. quantity of oxygen, $K_2O_2.O_2+CO=K_2O_2.CO+O_2$." Dry **carbon dioxide** has no action at ordinary temp., but when heated to about 100°, alkali carbonate and oxygen are formed: $2K_2O_4+2CO_2=2K_2CO_3+3O_2$. **Phosphorus** reacts vigorously, forming the alkali phosphate; and with **sulphur,** the alkali sulphate and a little sulphide are formed; if sulphur vapour, carried along with a stream of nitrogen to moderate the vigour of the reaction, be led over the heated peroxide, sulphur dioxide, potassium sulphate, and polysulphide are formed. With **sulphur dioxide,** potassium sulphate and oxygen are formed; with **phosphine,** or **hydrogen sulphide,** the corresponding phosphide or sulphide are formed. **Nitrous oxide** does not decompose potassium peroxide; with sodium dioxide and **nitric oxide,** sodium nitrite is formed: $Na_2O_2+2NO=2NaNO_2$;

it might therefore be expected that potassium tetroxide would give the nitrate: $K_2O_4+2NO=2KNO_3$. This, however, is not the principal reaction, and A. V. Harcourt suggests that the reaction proceeds: $K_2O_4+2NO=K_2O_2+2NO_2$, followed by $K_2O_2+2NO=2KNO_2$, and by $K_2O_2+2NO_2=2KNO_3$. With **ammonia** gas, nitrogen and potassium hydroxide are formed. The peroxide oxidizes many **metals** with incandescence—*e.g.* potassium, arsenic, antimony, tin, zinc, and copper—while bismuth, lead, iron, silver, and even platinum are oxidized without incandescence. The aq. soln. oxidizes **manganous** salts to the peroxide; precipitates a yellow hydrated cupric peroxide from **cupric salts,** but if the potassium tetroxide be in excess, the cupric peroxide is reduced to the hydroxide.[41] Potassium tetroxide behaves like a reducing agent towards acid soln. of **potassium permanganate,** and it decomposes into hydrogen peroxide when treated with an acid without liberating ozone; this is shown by the fact that if indigo-sulphuric acid be present there is no bleaching of the colour as would occur if ozone were formed.

According to A. von Baeyer and V. Villiger,[42] solid potassium hydroxide is coloured an intense orange by **ozone**; and when ozone is passed into a 40 per cent. soln. of potash lye cooled by a freezing mixture the same colour is developed, but the colour disappears when the soln. is removed from the freezing mixture. Rubidium and cæsium hydroxides behave in a similar manner; but sodium hydroxide is coloured only a faint yellow; lithium is likewise slightly affected. According to W. Manchot and W. Kampschulte, liquid ammonia is coloured an intense orange-red which vanishes when the temp. rises. A. von Baeyer and V. Villiger, and A. Bach, assumed that the alkali tetroxides are formed, and that these oxides are really salts—**ozonates**—of what they call **ozonic acid,** H_2O_4, or $(HO)_2=O=O$, the hydroxyl derivative of ozone, $O=O=O$. According to W. Traube, when freshly prepared, the ozonate yields oxygen and very little hydrogen peroxide, when kept at the ordinary temp. for a short time, or at 90°–100° the ozonate becomes paler in colour and yields a larger amount of hydrogen peroxide when treated with water or an acid. W. Traube suggests that the change is due to an intramolecular transformation of the ozonate first formed to a tetroxide, and he formulates the tetroxide $KO.O.KO_2$, where the O_2 group is held by auxiliary valencies, and is released on treatment with water, while the residual KOOK forms hydrogen peroxide; the oxonate is formulated $(KOH)_2O_2$. The slow change from ozonate to tetroxide is due to the oxidation of the KOH-group by the oxygen: $3(KOH)_2O_2=2(K_2O_2.O_2)+2KOH+2H_2O$. This agrees with the fact that the ozonates and the tetroxides are peculiar in yielding indifferent oxygen when dissolved in water. W. Traube made a quantitative study of the reaction between ozone and potassium hydroxide, and W. Strecker and H. Thienemann studied the action of ozone on soln. of the sodium, potassium, rubidium, and cæsium in liquid ammonia, and obtained the ozonates or ozonides contaminated with products of the action of ozone on ammonia.

E. Schöne (1878)[43] precipitated crystals of **hydrated alkali peroxides** by adding alcohol to the soln.; by varying the relative proportion of alkali peroxide and hydrogen peroxide in the soln., he claims to have prepared compounds corresponding with $Na_2O_2.8H_2O$, or $Na_2H_4O_6.4H_2O$, that is $Na_2O_4.6H_2O$, or $Na_2O_2.2H_2O_2.4H_2O$; and also $K_2H_4O_4$, or $2KOH.H_2O_2$, or $K_2O_2.2H_2O$ by evaporating an aq. soln. of potassium tetroxide or a mixture of eq. amounts of potassium hydroxide and hydrogen peroxide over conc. sulphuric acid in a good vacuum; and $K_2H_4O_6$ or $K_2O_4.2H_2O$ by evaporating an aq. soln. of a mol. of potassium hydroxide with three mols. of hydrogen peroxide in a good vacuum over conc. sulphuric acid at a temp. below 0°.

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§ 11. Hydroxides of the Alkali Metals

In an important paper entitled: *Experiments upon magnesia alba, quicklime, and other alcaline substances*, published in 1755,[1] J. Black first made clear the relations between **caustic alkali** and **mild alkali**; that is, between the alkali hydroxides and alkali carbonates. These relations were not understood by the early chemists. They believed the mild alkalies and alkaline earths—that is, the carbonates of the alkalies and alkaline earths—to be elementary substances; that the causticity of lime was due to the union of fire-matter or phlogiston with elemental chalk; and the conversion of mild alkali into caustic alkali, with the simultaneous regeneration of chalk, by boiling the former with caustic lime, was due simply to the transfer of the phlogiston or fire-matter from the lime to the mild alkali. Otherwise expressed: Quicklime=Chalk+Fire-matter. J. Black proved this hypothesis to be untenable. H. L. Duhamel du Monceau [2] had shown nine years earlier in a memoir: *Diverses expériences sur la chaux*, that limestone loses weight when calcined and regains it little by little on exposure to air.

J. Black demonstrated experimentally that chalk after ignition neutralized the same quantity of acid as before ignition, but the calcined chalk dissolves in the acid without effervescence, whereas the original chalk lost a gas which he called *fixed air*, but which is now called carbon dioxide. W. Homberg [3] had previously demonstrated the same fact in 1700, and used it as an argument against the prevailing hypothesis that chalk loses its alkalinity or alkaline force by calcination.

The salts formed by the action of acids on calcined and uncalcined lime were shown to be identical in every respect, and the same amount of gas was expelled from chalk whether the chalk be calcined or digested in acids. Further, by weighing the chalk before and after calcination, J. Black found a *loss*, not a gain in weight. Thus:

Ordinary chalk	120 grains
Quicklime	68 ,,
Loss in weight	52 ,,

Hence, added J. Black, "we may safely conclude that the volatile matter lost during the calcination is mostly air, and hence calcined lime does not emit air or make any effervescence when mixed with acids." Again, lime becomes caustic owing to the loss of fixed air. Consequently, J. Black proved that Chalk=Quicklime+Fixed air. Hence, quicklime is simpler than chalk or limestone.

Joseph Black thus showed the phlogiston hypothesis to be a gratuitous assumption in explaining the transformation of limestone into caustic lime, before A. L. Lavoisier attempted to apply J. Black's idea to processes of oxidation and combustion.[4]

J. Black found that the quicklime was converted back into chalk by exposure to air, and further that

> Quicklime does not attract air when in its ordinary form, but is capable of being joined to one particular species only, which is decomposed through the atm., either in the shape of an exceedingly subtle powder, or more probably in that of an elastic fluid. To this I have given the named *fixed air*.

J. Black also succeeded in transferring the fixed air from potashes to quicklime, for, on boiling the 68 grains of quicklime in the experiment cited above with potashes, he finally obtained 118 grains of a white powder "similar in every trial" to ordinary chalk. The 118 grains of chalk correspond with the 120 grains originally taken within limits of experimental error. The resulting caustic potashes no longer effervesced with acids, whereas the regenerated chalk did. Hence J. Black concluded that the potashes were made caustic by the transfer of fixed air contained

in potashes to the caustic lime. Somewhat similar results were obtained with magnesia and its carbonate as were obtained with lime and its carbonate. Joseph Black did not attempt to find the nature of the aeriform substance, but he did demonstrate the modern view of the changes which attend the transformation of a mild into a caustic alkali, and proved that these changes are similar to those which occur during the conversion of a mild earth into a quicklime. Black's experiments also made clear the relations between the mild alkalies (alkali carbonates); caustic alkalies (alkali hydroxides); mild earths (carbonates of the alkaline earths); and the *quicklimes* (oxides of the alkaline earths).

C. W. Scheele (1784) said that Black's experiments were so solid and convincing that it seems impossible to form any objection to them. The balance enabled J. Black to perceive the invisible, so to speak, and to open to chemistry a new era by brilliantly demonstrating the importance of *quantity*. Except for a few desultory experiments, chemistry, prior to J. Black, had laboured only with *qualities*. Lavoisier certainly must have recognized the part which Joseph Black had played in weakening the hold which phlogiston had obtained in chemistry. This engine of research—the balance—was again employed by A. L. Lavoisier in his brilliant work on oxidation and combustion. Enthusiasts have claimed for Lavoisier the introduction of the balance in chemistry. This is of course all wrong. The balance had been in use centuries earlier, and it is even depicted on the monuments of ancient Egypt. T. Bergmann, also, about this time, emphasized the use of the balance when he said:

> The balance is of singular service in investigating the properties of bodies, and in directing those properties to their proper uses. All effects are exactly proportioned to their causes; therefore, unless their mutual relations be examined by accurate trials, theory must be lame and imperfect.

Up to the time of the discovery of the alkali metals by H. Davy, potassium and sodium hydroxides—*caustic potash* and *caustic soda*—were considered to be oxides. J. P. J. D'Arcet (1808)[5] showed that *lapis causticus*—caustic alkali—contains another constituent which C. L. Berthollet proved to be water. J. L. Gay Lussac and L. J. Thénard, and H. Davy determined the exact proportion of water present in these compounds. According to Pliny's *Historia naturalis* (**31.** 46), it was the custom in the first century of our era to adulterate Egyptian *nitrum* with *calce*—lime. Consequently, the strengthening of the lye obtained from wood ashes by the addition of quicklime was probably known to the ancients, at any rate the formation of caustic lye is mentioned by Paulus Ægineta, a medical writer of the seventh century; and the preparation of caustic alkali is described by the Latin Geber, and by Albertus Magnus, in the thirteenth century. In essence, the same process is used to-day. Albertus Magnus said in his *Composition de compositis*:

> Grind very finely a considerable amount of the ashes from the rotten oak tree—*quercus putrida*—and mix them intimately with a sixth part of quicklime. Place a thick cloth over a cask, and on this put the mixture of ashes and lime. Pour boiling water over the mixture, and wash the ashes well. Allow the lye to settle in the cask until the next day. *Clarify by filtration. Boil down the lye in a cauldron until all the water has evaporated* and fumes are no longer evolved. Let the mass cool, and there will remain a hard stone which is called *alcali*.

G. E. Stahl[6] also showed in 1702 that caustic alkali is formed when nitre is decomposed by the metals.

Sodium and potassium oxides cannot be conveniently made by calcining the corresponding carbonate and digesting the residue with water as is possible in the case of calcium oxide, because the two alkali carbonates do not decompose so readily on ignition as calcium carbonate. Lithium carbonate, however, is more closely related to calcium carbonate than the other alkali carbonates. The preparation of the oxides of potassium and sodium is rather difficult and expensive.

Hence, although the hydroxide can be made by the action of water on the oxide, it is far more economical to employ a method of preparation based on that described by Albertus Magnus. The chloride is first converted into carbonate by Leblanc's or Solvay's process, and the carbonate is subsequently converted into the hydroxide by causticization with lime. If the alkali chloride could be transformed directly into the hydroxide, withont the intermediate formation of the carbonate, by a cheap enough process, the waste of industrial energy, so to speak, involved in this roundabout procedure would be avoided. Numerous patents [7] have been obtained for decomposing common salt by steam or superheated steam, but without any useful result.

In C. E. Acker's process [8] for sodium hydroxide, fused sodium chloride was electrolyzed with a molten lead anode; the resulting alloy of sodium and lead was decomposed by steam to form hydrogen and sodium hydroxide. Chlorine and hydrogen were thus obtained as by-products. In spite of this advantage, the process could not compete successfully with that ordinarily employed. There are also numerous forms of electrolytic cell in which brine is electrolyzed for chlorine, with sodium hydroxide as by-product. The cells are arranged so that the chlorine at the anode does not mix with the hydrogen and alkali hydroxide formed at the cathode.[9] These processes can be profitably employed where the required electrical energy is cheap enough. M. H. van Laer investigated the possibility of using sodium or potassium carbonate in place of sodium chloride for the manufacture of the alkali hydroxide. S. S. Sadtler produced sodium hydroxide by the action of calcium hydroxide on sodium hydrophosphate.

There are also chemical processes for the direct conversion of the chloride into hydroxide. For example, in 1773, C. W. Scheele found that when sodium or potassium chloride is boiled with lead oxide or hydroxide,[10] a quantitative yield of the alkali hydroxide is obtained, and a yellow basic lead chloride, $3PbO.PbCl_2$, is precipitated: $2NaCl+4PbO+H_2O=2NaOH+3PbO.PbCl_2$. Lead oxychloride is used as a yellow pigment, and the process of preparing this substance as the main product of the reaction was patented in 1781 by J. Turner—hence the name *Turner's yellow*. It has been recently proposed to work this process for the alkali hydroxide on a manufacturing scale; but there is a long list of sterile patents for this reaction dating from 1773 up to recent times.[11] The process has also been the subject of critical investigation by J. F. A. Göttling (1781), F. R. Curaudau (1792), R. C. Clapham (1859), etc. The lead can be recovered in the following manner: The basic lead chloride is separated from the lye, dissolved in nitric acid, and evaporated down. The hydrogen chloride which is evolved is condensed, and the lead nitrate is dissolved in water, and lead hydroxide is precipitated by the addition of ammonia. The chief difficulty with the process lies in the recovery of the lead oxide in a suitable form. According to F. M. Bachet, the lead oxychloride can be decomposed by lime water: $3PbO.PbCl_2+Ca(OH)_2=4PbO+CaCl_2+H_2O$, and the residual mixture of lead oxide and calcium chloride used over again.[12]

C. Löwig [13] proposed to roast the alkali carbonate with ferric oxide in a reducing atm. whereby sodium ferrite, $NaFeO_2$, is formed: $Na_2CO_3+Fe_2O_3=2NaFeO_2+CO_2$. When the resulting cake is treated with water, caustic soda is formed and the ferric oxide (or hydroxide) is regenerated: $2NaFeO_2+H_2O=Fe_2O_3+2NaOH$. However, the process of causticizing the carbonate with lime appears in the main to have prevailed against other proposals. Suggestions have been made to caustify nitre cake; [14] and B. Neumann and E. Karwat have discussed the causticization of alkali sulphates.

Sodium or potassium hydroxide can be taken as a type of the process for the caustification of alkali carbonate by lime. When calcium hydroxide is added to a boiling soln. of sodium carbonate in an iron, or silver, or nickel vessel, calcium carbonate is precipitated, and sodium hydroxide, NaOH, remains in soln.: $Ca(OH)_2+Na_2CO_3=2NaOH+CaCO_3$. The clear soln. is decanted from the precipitated calcium carbonate, and conc. by heating it in iron pots. The reaction

between alkali carbonate and calcium hydroxide has many points of interest. It is best studied in the light of the theory of equilibrium, so useful in the study of chemical reactions generally. When potassium carbonate and slaked lime are used there are four salts in soln. and in equilibrium ;[15] accordingly, the reaction is represented : $K_2CO_3+Ca(OH)_2\rightleftharpoons CaCO_3+2KOH$.

Molecular theory of caustification.—An excess of solid calcium hydroxide is supposed to be present at the start, so that as fast as calcium hydroxide is removed *from* the soln. by reacting with the potassium carbonate, more passes *into* soln. Thus the conc. of the calcium hydroxide in the soln. is kept constant. The solubility of calcium carbonate is very small, and, in consequence, any calcium carbonate in excess of the solubility will be precipitated as fast as it is formed. The reaction proceeds steadily from right to left because, all the time, calcium hydroxide steadily passes into soln., and calcium carbonate is steadily precipitated ; but the solubility of calcium carbonate steadily increases with increasing conc. of potassium hydroxide. There is a steady transformation of the potassium carbonate into potassium hydroxide in progress. The conc. of the potassium carbonate is steadily decreasing, while the conc. of the potassium hydroxide is steadily increasing. Consequently, when the potassium hydroxide has attained a certain conc. so much calcium carbonate will be present in the soln. that the reaction will cease. Hence the conc. of the potassium carbonate should be such that it is all exhausted before the state of equilibrium is reached. If the conc. of the potassium hydroxide should exceed this critical value, the reaction will be reversed, and calcium carbonate will be transformed into calcium hydroxide.

M. le Blanc and K. Novotny showed, for example, that at 100°, the percent. of sodium carbonate transformed into hydroxide is greater with normal than with ternormal soln. Thus, for equilibrium,

Initial conc., Na_2CO_3 . .	N-	$2N$-	$3N$-sol.
Percentage transformation .	99·1	97·8	93·2

They also found the yield to be independent of the temp. so that the heat of the reaction is virtually zero, and no improvement can be expected by working at higher temp. under press., as was proposed by E. W. Parnell[16] in 1877. According to G. Bödlander and R. Lucas, the hydroxides of barium and strontium are more soluble than calcium hydroxides, while the carbonates are less soluble than calcium carbonate. Hence, better yields are obtained with these hydroxides. With strontium hydroxide, the reaction is exothermal, so that the yield should be increased by working at lower temp.

Ionic theory of caustification.—The explanation offered by the ionic theory runs somewhat as follows : At the start, the soln. contains the ions

$$K_2CO_3\rightleftharpoons 2K^{\cdot}+CO_3'' \text{ ; and } Ca(OH)_2\rightleftharpoons Ca^{\cdot\cdot}+2OH'$$

The solubility product $[Ca^{\cdot\cdot}][CO_3'']$ is very small, and very much less than the solubility product $[Ca^{\cdot\cdot}][OH']^2$; consequently, since relatively large proportions of both the ions $Ca^{\cdot\cdot}$ from the $Ca(OH)_2$, and CO_3'' from the K_2CO_3, are present in the soln., calcium carbonate will be precipitated, and will continue being precipitated as long as the potassium carbonate and calcium hydroxide can supply ions CO_3'' and $Ca^{\cdot\cdot}$ in excess of the solubility product of calcium carbonate. But the calcium hydroxide furnishes the $Ca^{\cdot\cdot}$ ions, and the solubility of $Ca(OH)_2$ is largely determined by the solubility product $[Ca^{\cdot\cdot}][OH']^2$. With the steady removal of $Ca^{\cdot\cdot}$ and CO_3'' ions, the conc. of the $K^{\cdot}$ and the OH' ions must be continually increasing. By-and-by the conc. of the OH' ions becomes relatively large ; this, in virtue of the common ion OH', reduces the conc. of the $Ca^{\cdot}$ ions required to maintain the solubility product of calcium hydroxide up to its own constant value. Finally, when the conc. of the OH' ions is so great that the conc. of the $Ca^{\cdot\cdot}$ ions from the calcium hydroxide is no greater than the conc. of the $Ca^{\cdot\cdot}$ ions required to maintain

the solubility product of the calcium carbonate at its own characteristic value, the reaction will stop. Hence the conc. of the potassium carbonate in the soln. should be so adjusted that this salt is exhausted before the reaction stops.

There is a complication in causticizing sodium carbonate by means of lime owing to the formation of hydrated crystals of *gaylussacite*, $CaNa_2(CO_3)_2.5H_2O$; and of anhydrous $CaNa_2(CO_3)_2$. The latter is stable above 40°, the former below 40°. These salts are sparingly soluble, and they are precipitated along with the lime sludge with a consequent loss of soda. The double salts are stable in soln. with conc. of sodium carbonate exceeding certain limits, and they are decomposed by pure water. Consequently, the soda could be recovered by repeatedly washing the precipitated sludge, but, in practice, this is not expedient because the recovered soln. would be too dil. for profitable conc. M. H. van Laer found soln. of sodium carbonate is readily converted into the hydroxide by the electrolysis of aq. soln. in the presence of an oxy-salt like the sulphate, chlorate, or nitrate.

In 1818, A. Arfvedson [17] causticized lithium carbonate by means of calcium hydroxide, but the sparing solubility of lithium carbonate causes but a poor yield. L. Troost made the hydroxide by dissolving in water the oxide obtained by the combustion of the metal ; and C. G. Gmelin decomposed lithium sulphate by an eq. soln. of barium hydroxide. In either case, the soln. should be evaporated rapidly to dryness in a silver vessel, and then fused.

The alkali hydroxides can be obtained from the alkali *sulphate* by treating it with baryta water [18] or strontia water, whereby insoluble barium or strontium sulphate is precipitated, and the alkali hydroxide remains in soln. : $Ba(OH)_2+K_2SO_4=BaSO_4+2KOH$; or by treating a sat. soln. of the alkali sulphate with calcium sulphate there is a partial conversion of sulphate to hydroxide. The sulphate can also be converted to the phosphate by treatment with acid calcium phosphate ; and by the addition of milk of lime, alkali hydroxide is formed. The alkali *nitrate* can be causticized by ignition with carbon, copper turnings, or iron oxide, and subsequently extracting the liquid with water. The product is impure. Numerous processes for causticizing the *alkali chloride* have been proposed.

The purification of the alkali hydroxides.—Numerous impurities have been reported in commercial sodium and potassium hydroxides. Several have commented on the presence of peroxide, particularly in caustic potash.[19] Various salts—carbonate, sulphate, nitrate, nitrite, chloride, and phosphate—as well as alumina, silica, organic matters, and metal oxides—*e.g.* arsenic, vanadium, iron, etc., have been reported. More or less of the other alkalies may also be present.

The so-called potassium or sodium hydroxide *pure by alcohol* [20]—*e.g. soude à l'alcool*—was prepared by C. L. Berthollet in 1786 by dissolving the hydroxide in absolute alcohol. Most of the impurities remain undissolved, but a little chloride, carbonate, and acetate pass into the alcoholic soln. The alcoholic soln. is allowed to settle, the clear liquid is decanted off, and evaporated in a silver dish, on a water-bath. The resinous matter which is formed, is removed from the warm semi-solid mass by means of a silver spatula, and the mass is then poured on a plate of polished iron.

Alkali hydroxide of a high degree of purity can be made by treating the highly purified alkali carbonate with silver carbonate to remove the chlorides, and then boiling the clear liquid, in a silver dish, with lime made by the ignition of purified calcium carbonate. The soln. is then filtered through a layer of pounded marble which has been well washed to remove the powder. The liquid is then evaporated in a silver dish. The alkali-lye should not come in contact with glass on account of rapid corrosion. Alkali hydroxide soln. for volumetric analysis are often made by the action of the metal on water, or water vapour.[21] The metal is supported in a nickel gauze funnel over water contained in a basin. The water vapour attacks the sodium slowly and a soln. of the hydroxide can be collected in a silver or nickel basin placed underneath. All is covered by a bell-jar. The hydrogen escapes through the water under the bell-jar. The lye which collects in the basin contains about 40 per cent. NaOH.

Properties of the alkali hydroxides.—The alkali hydroxides are brittle, white, translucent solids with a more or less crystalline fracture, and fibrous texture. Sodium hydroxide deliquesces on exposure to the air, but it goes solid again owing to the formation of the carbonate by the absorption of carbon dioxide from the air. Lithium hydroxide is a little hygroscopic. Potassium hydroxide is even more deliquescent than the sodium compound; but its carbonate is also deliquescent. The hydroxides are very soluble in water, and they also dissolve in alcohol. The reported numbers for the **specific gravities**[22] of sodium hydroxide range from 1·723 to 2·130; and for potassium hydroxide, from 1·958 to 2·6. The best representative sp. gr. are 2·54 for lithium hydroxide; 2·130 for sodium hydroxide; 2·044 for potassium hydroxide; 3·203 (11°) for rubidium hydroxide; and 3·675 (11°) for cæsium hydroxide.

R. de Forcrand found the **melting point** of lithium hydroxide to be 445°, and G. Scarpa, 462°. The hydroxide remains undecomposed[23] at this temp., but at a higher temp. some decomposition occurs: $2LiOH = Li_2O + H_2O$. According to G. von Hevesy, sodium hydroxide melts at 318·4° ± 0·2°, meaning that the observed numbers vary between 318·2° and 318·6°. This does not necessarily mean that this constant is known to these limits of accuracy unless the purity of the material be unimpeachable. G. Scarpa gives 310° as the melting and 290° as the solidification temp.; B. Neumann and E. Bergve give 300° as the solidification temp. Sodium hydroxide volatilizes unchanged at high temp. Potassium hydroxide melts at 360·4° + 0·7°. G. Scarpa gives 380° as the m.p., and 260° as the transformation point; B. Neumann and E. Bergve give the m.p. 345°. Rubidium hydroxide melts at 301° ± 0·9°; and cæsium hydroxide at 272·3° ± 0·3°. G. von Hevesy found that the four hydroxides show terraces in the cooling curves below their m.p. The **dissociation pressures** of lithium hydroxide at different temp. are 9·2 mm. at 561°; 92 mm. at 700°; 234 mm. at 782°; 526 mm. at 875°; and 760 mm. at 924°. The dissociation press. measured by J. Johnston[24] were not considered satisfactory. D. D. Jackson and J. J. Morgan found the **vapour pressure** of potassium hydroxide to be 8 mm. of mercury at 795°, and the relative volatility of different potassium compounds is in decreasing order: hydroxide, chloride, oxide from carbonate, sulphate, and natural silicates.

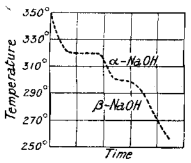

FIG. 17.—Cooling Curve of Sodium Hydroxide.

The cooling curve for sodium hydroxide is illustrated in Fig. 17. The **transition point** from *α- to β-sodium hydroxide* is 299·6° ± 0·5°, that is, 19° below the m.p.; from *α- to β-potassium hydroxide*, 248° ± 0·5°, that is, 112° below the m.p.; from *α- to β-rubidium hydroxide*, 245° ± 0·5°, that is, 40° below the m.p.; and from *α- to β-cæsium hydroxide*, 223° ± 0·5°, that is, 49° below the m.p.

The **latent heat of fusion** of sodium hydroxide per gram is 40·0 cals.; potassium hydroxide, 28·6 cals.; rubidium hydroxide, 15·8 cals.; and cæsium hydroxide, 10·7 cals. The corresponding values in calories per mol. are 1602, 1606, 1614, and 1609 cals. respectively. The **heat of transformation** of sodium hydroxide per gram is 24·7 cals.; potassium hydroxide, 27·1 cals.; rubidium hydroxide, 16·8 cals.; and cæsium hydroxide, 11·8 cals. The corresponding values in calories per mol. are 990, 1522, 1702, and 1763 cals. respectively.

Molten sodium and potassium hydroxides are completely miscible in all proportions, and the f.p. curve has a minimum at 187° with a mixture containing 38·7 atomic per cent. of KOH, that is, 48·97 per cent. of KOH by weight. The transformation temp. of the cooling solid alloys furnish a curve similar in form to the f.p. curve, and the solid eutectic has a transformation point at 181°. Mixtures of potassium and rubidium hydroxides are completely miscible, and they give a curve with two maxima; one rises from the m.p. of potassium hydroxide 360·4° up to 399° with 87 atomic per cent. of KOH, and the other from the m.p. of rubidium hydroxide

301° up to 351° with 22·3 atomic per cent. of KOH. The intervening minimum is at 306° with 65·6 atomic per cent. of KOH. There is no evidence to show that the maxima represent definite compounds. The transition temp. of the cooling solid alloy furnish an analogous curve. Sodium and rubidium hydroxides are not miscible between 8·8 and 37·6 atomic per cent. of the latter hydroxide. There is a maximum on the curve at 278° and 30·7 atomic per cent. of rubidium hydroxide which may or may not correspond with the formation of a compound RbOH.2NaOH. The two minima in the m.p. curve are near 237° with about 83 and 48 atomic per cent. of rubidium hydroxide.

The **heat of formation of the alkali hydroxides**:[25] R+O+H=ROH, is between 111·0 and 117·3 Cals. for lithium, 101·87 to 102·7 Cals. for sodium, 101·7 to 103·17 Cals. for potassium, 101·99 Cals. for rubidium, and 101·31 Cals. for cæsium hydroxide. The thermal value of the reaction R+O+H+aq=ROHaq is 117·5 Cals. for lithium; 111·8 to 112·5 Cals. for sodium; and 116·5 to 117·1 Cals. for potassium hydroxide. The heat of the reaction 2R+O+aq=2ROHaq is 166·0 to 166·52 Cals. for lithium; 144·2 to 155·26 Cals. for sodium; 159·8 to 164·56 Cals. for potassium; 164·8 Cals. for rubidium; and 172·13 for cæsium hydroxide. The heat of the reaction $2R+O+H_2O=2ROH$ is 135·38 Cals. for sodium, and 137·98 Cals. for potassium. The heat of the reaction $R_2O+H_2O+aq=2ROHaq$ is between 56·5 and 63·9 Cals. for sodium; 67·4 to 75·0 Cals. for potassium; 80·0 Cals. for rubidium; and 72·15 to 80·6 Cals. for cæsium. The heat of formation of an aq. soln. of the hydroxide by the action of the metal on water has been discussed in connection with the metals. The **heat of solution** of the alkali hydroxides[26] depends on the amount of water with which they are mixed. The heat of dilution of lithium hydroxide LiOH with 111 mols. of water is 4·147 Cals., and with $400H_2O$, 5·8 Cals.—R. de Forcrand gives 4·477 Cals. for the heat of soln. at 24°. J. Thomsen found the heat of soln. of a mol. of $KOH.3H_2O$ or of $NaOH.3H_2O$ in n mols. of water to be in large calories:

n	2	4	6	17	22	47	97	197
$KOH.3H_2O$ . .	1·50	2·10	2·36	2·68	—	2·74	2·75	2·78
$NaOH.3H_2O$ . .	*2·13*	*2·89*	*3·09*	*3·28*	*3·26*	*3·11*	*3·00*	*2·94*

The thermal effect is positive for both hydroxides. If a start be made from the anhydrous oxides, n in the tables must be increased by 3, and 13·29 Cals. added to the numbers for potassium hydroxide, and 9·94 Cals. to the numbers for sodium hydroxide. There is a maximum with sodium hydroxide corresponding with $NaOH+20H_2O$, so that if a soln. containing more than this amount of water is diluted, there will be an absorption of heat. M. Berthelot investigated this subject further, and found that on adding 41 mols. of water to a mixture $KOH+3·6H_2O$, +2·41 Cals. were developed; with the addition of $50H_2O$ to $KOH+4·11H_2O$, +1·44 Cals., with $60H_2O$ to the mixture $KOH+11·0H_2O$, +0·16 Cals. If water, $17H_2O$, be added to a soln. containing $KOH+15·3H_2O$, 0·045 Cals. are evolved, but with the addition of $79H_2O$ to the initial mixture, 0·035 Cals. are absorbed, and heat is absorbed by the dilution of soln. containing more water than is represented by $KOH+32·3H_2O$, thus, the thermal value of the dilution of this mixture $21H_2O$ is —0·035 Cals., and of the mixture $KOH+55·3H_2O$ with $56H_2O$, —0·026 Cals. Similar remarks apply to sodium hydroxide, a soln. of NaOH in nH_2O at 10°–12° develops $23n^{-2}$ Cals. on dilution with $(200-n)H_2O$, when n lies between 2·5 and 5·6; $(23n^{-2}-11·5n^{-1})$ Cals. for n between 5·6 and 18·4; and $-11·5n^{-1}$ Cals., when n is greater than 18·4. Similarly, for potassium hydroxide at 15°, the heat of dilution is $23n^{-2}$ Cals. when n, the number of mols. of water in which the hydroxide is dissolved, is not greater than 11; between $n=11$ and $n=32$, the heat of dilution is $(23n^{-2}-2·3n^{-1})$ Cals.; and when n exceeds 32, the heat of dilution is $-2·3n^{-1}$ Cals. For the heat of dilution: $CsOH+320H_2O$, N. N. Beketoff gives +15·88 Cals., and for the dilution of rubidium hydroxide with an excess of water, R. de Forcrand

gives 14·264 Cals. at 15°, and for cæsium hydroxide, 16·423 Cals. F. R. Pratt has investigated the heats of dilution of soln. of sodium and potassium hydroxides.

J. T. Lōwitz found the solubility of potassium hydroxide to be such that it dissolved in half its weight of water; A. Bineau found water dissolved two-thirds its weight of sodium hydroxide, and its own weight of potassium hydroxide; and J. Dalton compiled the first table of the solubility of the last-named compound. H. Schiff, and G. T. Gerlach calculated solubility tables from Dalton's data. The **solubility curve** [27] of lithium hydroxide has a eutectic at −18° with 11·2 per cent. of lithium hydroxide; at −59°, the soln. contains 4·31 per cent. LiOH; and the solid phase with ice, at the eutectic, is the **monohydrate of lithium hydroxide,** $LiOH.H_2O$, of sp. gr. 1·829; it has a heat of soln. of 0·720 Cal. at 18°. The solubility of the monohydrate is:

	10·0°	45·5°	60·0°	77·3°	80·0°	100°
Per cent. LiOH . .	11·28	11·68	12·25	13·01	13·27	14·90

The existence of C. Göttig's $LiOH.\frac{1}{2}H_2O$ precipitated from alcoholic soln. has not been confirmed. According to W. Dittmar, the percentage amount of Li_2O in sat. aq. soln. of lithium hydroxide at temp. θ can be represented by $6·6750+0·003466\theta+0·0003\theta^2$. The solubility curve of sodium hydroxide,[28] Fig. 18, shows the conditions under which the mono-, di-, tri-, tetra-, penta-, and hepta-hydrated sodium hydroxides are stable. The anhydrous hydroxide passes into the **monohydrated sodium hydroxide,** $NaOH.H_2O$, below 64·3°; and the monohydrate is deposited when a hot soln. of the hydroxide is cooled. The monohydrate passes into the **dihydrate of sodium hydroxide,** $NaOH.2H_2O$, at 12·3°. The same hydrate is obtained from a 96 to 97 per cent. soln. in alcohol. The dihydrate passes into the $3\frac{1}{2}$-hydrate, $NaOH.3·5H_2O$, at 5°, or continues down to −1·3°, when it passes into the **trihydrated sodium hydroxide,** $NaOH.3H_2O$ (or possibly $3·1H_2O$); the trihydrate at −3° passes into the **β-tetrahydrated sodium hydroxide,** β-$NaOH.4H_2O$; and this, at −12·3°, into the **pentahydrated sodium hydroxide,** $NaOH.5H_2O$, which forms a eutectic with ice at −32° and 19·8 per cent. of NaOH.

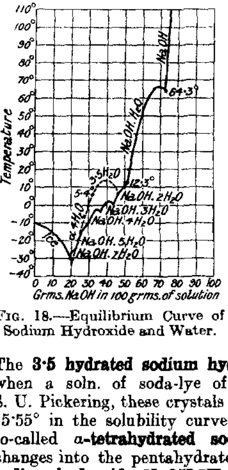

FIG. 18.—Equilibrium Curve of Sodium Hydroxide and Water.

The **3·5 hydrated sodium hydroxide** is deposited in tabular monoclinic crystals when a soln. of soda-lye of sp. gr. 1·365 is cooled to −8°. According to S. U. Pickering, these crystals melt at 15·5°, corresponding with the maximum at 15·55° in the solubility curve; this curve has a slight break at 5·4°, when the so-called **α-tetrahydrated sodium hydroxide,** α-$NaOH.4H_2O$, appears. This changes into the pentahydrate at −18°, and this in turn into the **heptahydrated sodium hydroxide,** $NaOH.7H_2O$ at −24°; the heptahydrate forms a eutectic with ice at −28°, and 19 per cent. of NaOH. It is convenient to take for the solubility of sodium hydroxide in 100 grms. of soln.:

	0°	10°	20°	30°	40°	60°	80°	110°
NaOH	29·6	34·0	52·2	54·3	56·3	63·5	75·8	78·5

The solubility of sodium hydroxide at −20° is 16·0, and at 192°, 83·9. The solubility curve of potassium hydroxide [29] shows the existence of the mono-, di-, and tetra-hydrates. There is a eutectic near −66° with a 30 per cent. KOH soln. between ice, and **tetrahydrated potassium hydroxide,** $KOH.4H_2O$, which passes into **dihydrated potassium hydroxide** at about −32·7°. The dihydrate is deposited when conc. aq. soln. are cooled. The small acute rhombohedral crystals melt at

about 35·5°, and they were described by P. Walter [30] in 1836. The dihydrate passes into the large radiating crystals of **monohydrated potassium hydroxide** at 32·5°, and these become anhydrous at about 143°. The solubility of potassium hydroxide grams per 100 grms. of soln. is:

	−65·2°	−32·7°	0°	10°	20°	30°	32·5°	100°	143°
KOH . .	30·8	43·8	49·2	50·7	52·8	55·76	57·44	64·03	75·73
	$KOH.4H_2O$			$KOH.2H_2O$			$KOH.H_2O$		

According to W. H. Schramm, an evolution of gas is sometimes noticed when fused sodium hydroxide is dissolved in water; the greater quantity of this gas is air contained in the hydroxide; an excess of oxygen may be present. This is thought to be due to the decomposition of an alkali compound of a higher ferric oxide, say *sodium perferrite*, $Na_2O.Fe_2O_4$, which is possibly formed: $2NaOH+O_2=Na_2O_2+H_2O_2$; $Na_2O_2+Na_2O.Fe_2O_3=Fe_2O_4.Na_2O+Na_2O$; and $Na_2O.Fe_2O_3+H_2O_2=H_2O+Na_2O.Fe_2O_4$. The pungent odour of the gas is possibly due to the mechanical carrying of sodium hydroxide soln. by the bubbles of gas.

The rubidium hydroxide of commerce [31] is a **monohydrated rubidium hydroxide,** $RbOH.H_2O$, which melts at 145°, and at 350° it is completely dehydrated to RbOH. At a higher temp. it begins to peroxidize and attack the crucible. The heat of soln. of the monohydrate is 3·702 Cals. at 15°. The commercial cæsium hydroxide is likewise a **monohydrated cæsium hydroxide,** $CsOH.H_2O$; it melts at 180°, and is completely dehydrated between 400° and 500°, and at the same time the mass begins to peroxidize. To prepare the pure hydroxide, it must be dehydrated in a current of dry hydrogen at 500°. The heat of soln. of the monohydrate is 4·317 at 15°.

According to F. A. H. Schreinemakers and A. Filippo,[32] 100 grms. of an aq. soln. of rubidium hydroxide contain 63·39 grms. RbOH at 30°; the corresponding numbers for potassium, sodium, and lithium hydroxides are respectively 55, 76, 54·3, and 11·27. Consequently, the solubilities of the alkali hydroxides increase as the at. wt. of the alkali metal increases.

The **specific gravities** of soln. of lithium hydroxide [33] at 18°, are:

Per cent. LiOH .	1·61	2·5	3·39	5·0	7·5
Sp. gr. . . .	1·0178	1·0276	1·0380	1·0547	1·0804

According to J. G. MacGregor, the volume of the aq. soln. of lithium hydroxide is smaller than that of the contained water. The sp. gr. of soln. of sodium and potassium hydroxide [34] with the corresponding percentage composition are indicated in Tables VI and VII. A sat. soln. of potassium hydroxide at 15° has a sp. gr. 1·5355, and has 51·7 per cent. of KOH. A normal soln. of sodium hydroxide at 18° has a sp. gr. 1·0418 (water at 4° =unity) and a normal soln. of potassium hydroxide under similar conditions has a sp. gr. of 1·0481. The *liquor potassæ* of the Pharmacopœia has a sp. gr. about 1·058, and contains about 5 per cent. of the hydroxide, KOH.

TABLE VI.—PER CENT. OF NaOH IN SOLUTIONS OF SODIUM HYDROXIDE OF SPECIFIC GRAVITY 1·00 TO 1·53 AT 15° (WATER AT 4° UNITY).

Sp. gr.	0	1	2	3	4	5	6	7	8	9
1·0	0	0·86	1·69	2·60	3·50	4·34	5·20	6·13	7·05	7·95
1·1	8·78	9·67	10·56	11·55	12·49	13·34	14·19	16·06	16·00	16·91
1·2	17·81	18·71	19·65	20·60	21·47	22·33	23·23	24·13	25·04	25·96
1·3	26·85	27·85	28·83	29·80	30·74	31·75	32·79	33·73	34·71	35·68
1·4	36·67	37·65	38·67	39·67	40·68	41·70	42·75	43·80	44·33	45·37
1·5	46·94	48·00	49·05	50·10	—	—	—	—	—	—

The influence of temp.[35] on the sp. gr. of soln. of sodium hydroxide is indicated

in Table VI. This gives an idea of the cubical expansion of these solns. when heated. The volume V of an aq. soln. of potassium hydroxide, which has a sp. gr. of 1·2738 at 0°, is $V=1+0{\cdot}0004150\theta+0{\cdot}000000577\theta^2$ for values of θ between 13° and 100°.

TABLE VII.—THE SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM HYDROXIDE AT DIFFERENT TEMPERATURES.

0° C.	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
1·367	1·362	1·357	1·353	1·348	1·342	1·336	1·331	1·326	1·321	1·316
1·357	1·352	1·347	1·343	1·337	1·332	1·327	1·322	1·316	1·311	1·306
1·347	1·342	1·338	1·333	1·327	1·322	1·317	1·312	1·306	1·301	1·296
1·338	1·332	1·328	1·323	1·317	1·312	1·307	1·302	1·296	1·291	1·286
1·328	1·322	1·318	1·313	1·307	1·302	1·300	1·292	1·286	1·280	1·274
1·318	1·313	1·308	1·303	1·297	1·292	1·286	1·281	1·275	1·269	1·263
1·308	1·303	1·297	1·292	1·287	1·282	1·276	1·271	1·265	1·259	1·253
1·298	1·293	1·287	1·282	1·277	1·272	1·266	1·261	1·255	1·249	1 242
1·288	1·283	1·277	1·272	1·267	1·262	1·256	1·251	1·245	1·239	1·232
1·278	1·273	1·267	1·262	1·258	1·252	1·247	1·242	1·236	1·231	1·225
1·268	1·263	1·257	1·252	1·248	1·242	1·237	1·232	1·226	1·221	1·215
1·257	1·252	1·247	1·242	1·238	1·233	1·228	1·223	1·218	1·213	1·207
1·247	1·242	1·237	1·232	1·228	1·223	1·218	1·213	1·208	1·203	1·197
1·237	1·232	1·227	1·222	1·218	1·212	1·208	1·202	1·198	1·192	1·187
1·227	1·222	1·217	1·212	1·208	1·202	1·198	1·192	1·188	1·182	1·177
1·217	1·212	1·207	1·203	1·198	1·192	1·189	1·184	1·179	1·173	1·168
1·207	1·202	1·197	1·193	1·188	1·184	1·180	1·175	1·169	1·163	1·158
1·197	1·192	1·187	1·183	1·178	1·174	1·169	1·164	1·158	1·153	1·147
1·187	1·182	1·177	1·173	1·166	1·164	1·159	1·153	1·148	1·143	1·137
1·176	1·172	1·167	1·163	1·156	1·154	1·149	1·143	1·138	1·132	1·127
1·166	1·162	1·157	1·153	1·146	1·144	1·139	1·133	1·128	1·122	1·117
1·156	1·152	1·148	1·144	1·137	1·135	1·130	1·124	1·118	1·113	1·107
1·146	1·142	1·138	1·134	1·127	1·125	1·120	1·114	1·108	1·103	1·097
1·136	1·132	1·128	1·124	1·118	1·116	1·110	1·104	1·099	1·093	1·087
1·126	1·122	1·118	1·114	1·108	1·106	1·100	1·094	1·089	1·083	1·077
1·115	1·112	1·108	1·104	1·099	1·097	1·091	1·086	1·080	1·074	1·068
1·105	1·102	1·098	1·095	1·090	1·087	1·082	1·076	1·070	1·064	1·058
1·094	1·091	1·088	1·086	1·080	1·078	1·073	1·067	1·061	1·056	1·048
1·084	1·081	1·078	1·076	1·070	1·068	1·063	1·057	1·051	1·046	1·040
1·074	1·071	1·068	1·066	1·060	1·058	1·053	1·047	1·042	1·036	1·030
1·064	1·061	1·058	1·056	1·050	1·048	1·043	1·037	1·032	1·026	1·020
1·054	1·051	1·048	1·046	1·040	1·038	1·033	1·027	1·021	1·013	1·010
1·044	1·041	1·038	1·036	1·030	1·028	1·023	1·017	1·011	1·006	1·000
1·034	1·031	1·028	1·026	1·020	1·018	1·013	1·007	1·001	0·996	0·990
1·024	1·021	1·018	1·016	1·010	1·008	1·003	1·997	0·991	0·986	0·980
1·014	1·011	1·008	1·006	1·000	0·998	0·993	0·984	0·981	0·976	0·970

TABLE VIII.—PER CENT. OF KOH IN SOLUTIONS OF POTASSIUM HYDROXIDE OF SPECIFIC GRAVITY 1·00 TO 1·54 AT 15° (WATER AT 4° UNITY).

	0	1	2	3	4	5	6	7	8	9
1·0	0	1·18	2·28	3·36	4·44	5·53	6·60	7·68	8·76	9·82
1·1	10·87	11·92	12·96	14·01	15·04	16·08	17·13	18·13	19·15	20·17
1·2	21·17	22·16	23·15	24·14	25·13	26·10	27·07	28·04	29·00	29·96
1·3	30·91	31·84	32·78	33·70	34·63	35·55	36·46	37·37	38·28	39·18
1·4	40·09	40·98	41·89	42·76	43·63	44·50	48·37	46·23	27·09	47·93
1·5	48·78	49·64	50·48	51·32	52·15	—	—	—	—	—

The **diffusion coefficients** of soln. of sodium and potassium hydroxides of different conc., between 12° and 13·5°, are, according to J. Thovert:[36]

	3·9	0·9	0·1	0·02 mols. per litre.
NaOH . .	0·985	1·045	1·11	1·12 cm. per day
KOH . .	2·43	1·86	1·72	1·68 „ „

The **viscosity** of aq. soln. of potassium and sodium hydroxides[37] are, according to A. Kanitz:

	1	*0·5*	*0·25*	*0·25 normal.*
NaOH . .	1·2355	1·1087	1·0560	1·0302
KOH . .	1·1294	1·0637	1·0313	1·0130

E. Briner represents the coeff. of viscosity of soln. of sodium hydroxide containing w grms. per litre at 20° by $0·010015+0·0000457w+0·000000321w^2$; and for potassium hydroxide, $0·010015+0·000018w+0·000000004w^2$. O. Pulvermacher also measured the viscosity of soln. of sodium hydroxide. W. C. Röntgen and J. Schneider[38] measured the **compressibility** of soln. of lithium and potassium hydroxide; Y. Schumann of sodium hydroxide; and O. Schmidt of potassium hydroxide.

The **boiling points** of soln. of the two hydroxides,[39] determined by G. T. Gerlach, are indicated in Table IX. The **vapour pressures** of aq. soln.[40] determined at 0°, also by G. T. Gerlach, are shown in Table X; and if p be the vap. press. of the solvent,

TABLE IX.—BOILING POINTS OF SOLUTIONS OF POTASSIUM AND SODIUM HYDROXIDES BETWEEN 100° AND OVER 300° FOR DIFFERENCES OF 10°.

Sodium Hydroxide.

	0°	*10°*	*20°*	*30°*	*40°*	*50°*	*60°*	*70°*	*80°*	*90°*
100	00	23·07	33·77	41·22	48·31	54·61	60·24	65·15	69·69	73·80
200	77·52	80·97	84·03	86·58	88·89	90·91	93·02	94·56	95·92	97·28
300	98·53	99·55	—	—	—	—	—	—	—	—

Potassium Hydroxide.

	0°	*10°*	*20°*	*30°*	*40°*	*50°*	*60°*	*70°*	*80°*	*90°*
100	00	25·65	36·51	43·42	48·05	51·57	54·88	57·80	60·42	62·73
200	64·93	66·89	68·73	70·67	42·46	74·07	75·76	77·52	79·05	80·32
300	81·63	82·99	84·03	85·11	86·16	—	—	—	—	—

TABLE X.—VAPOUR PRESSURES OF AQUEOUS SOLUTIONS OF SODIUM AND POTASSIUM HYDROXIDES AT 0°.

Sodium hydroxide.				Potassium hydroxide.			
Conc.		Relative lowering of vapour.	Vap. press. mm. Hg.	Conc.		Relative lowering of vap. press.	Vap. press. mm. Hg.
Grm. per 100 grm. water.	Normality.			Grms. per 100 rms. water.	Normality.		
5·42	1·355	0·0414	4·429	5·572	0·995	0·02832	4·489
11·78	2·945	0·1030	4·144	10·86	1·939	0·0571	4·356
20·50	5·125	0·2201	3·598	18·10	3·232	0·0933	4·196
27·24	6·810	0·3234	3·118	27·14	4·846	0·1557	3·898
35·18	8·795	0·4530	2·516	40·40	7·214	0·2495	3·470
47·44	11·86	0·6482	1·624	66·86	11·94	0·4386	2·593
59·60	14·90	0·7756	1·027	107·2	19·14	0·6655	1·547
				174·9	31·32	0·3614	0·638

p_s that of the soln., the relative lowering of the vap. press. is $(p-p_s)/p$. G. Tammann has also determined the lowering of the vap. press. of these soln. at 100°. The maximum vap. press. of a sat. aq. soln. of sodium hydroxide at 20° is 1·0 mm., and of potassium hydroxide, 0·8 mm. For 0·5 mols. of lithium hydroxide per kilogram of water at 100°, G. Tammann gives a lowering of the vap. press. of 15·9 mm. of mercury; and with 1·0 and 2·0 mols., a lowering of 37·4 mm. and 78·1 mm. respectively. C. Dieterici has measured the vap. press. of soln. of potassium hydroxide; and G. R. Paranjpe, of soln. of sodium and potassium hydroxides.

The **lowering of the freezing point**[41] of a 0·127N-soln. of lithium hydroxide is but half the normal value for LiOH, and it is therefore assumed that ionization is complete; the f.p. of sodium hydroxide falls 0·905° per gram of the hydrate $NaOH.2H_2O$ in 100 grms. of water, and not of the anhydrous hydroxide in soln.; and with potassium hydroxide, the f.p. falls 0·399° per gram of hydroxide in 100 grms. of water, and the lowering is not proportional to the amount of anhydrous hydroxide in soln., but rather to the amount of hydrate $KOH.4H_2O$.

The **specific heats** of aq. soln. of sodium and potassium hydroxides[42] are shown in Table XI. H. Hammerl represents the mol. ht. C of aq. soln. containing n mols. of water per mol. of KOH by the expression: $C=18n-28·08+421·11/n-1027·74/n^2$, and for NaOH, $C=18n+0·43+0·43+159·85/n-235·77/n^2$. According to T. W. Richards and A. W. Rowe, the sp. ht. of soln. of $KOH+100H_2O$ between 15·9° and 20·1° is 0·9568; of $NaOH+200H_2O$, 0·9827; of $NaOH+100H_2O$,

TABLE XI.—SPECIFIC HEATS OF AQUEOUS SOLUTIONS OF POTASSIUM AND SODIUM HYDROXIDES.

Sodium Hydroxide.

Per cent. R_2O.	n in $ROH.nH_2O$.	Sp. ht.	Mol. ht. C.	Mol. ht. nH_2O, C_1.	$C-C_1$.
38·34	80·9	0·816	66·0	40·9	+25·1
19·82	156·5	0·869	136·0	116·5	+19·5
7·21	430·1	0·924	397·4	390·1	+ 7·3

Potassium Hydroxide.

Per cent. R_2O.	n in $ROH.nH_2O$.	Sp. ht.	Mol. ht. C.	Mol. ht. nH_2O, C_1.	$C-C_1$.
32·72	143·5	0·697	100·0	87·5	+12·5
14·98	314·3	0·807	253·6	258·5	− 5·9
6·28	742·6	0·900	673·8	692·6	−18·8

0·9664; and of $LiOH+100H_2O$, 0·9813. The mol. ht. of the soln. $LiOH+100H_2O$ is 1791 cals., of $NaOH+100H_2O$, 1780 Cals., and of $KOH+100H_2O$, 1777, showing that the mol. ht. diminish as the at. wt. of the metal increases.

The **refractive indices** of aq. soln. of sodium and potassium hydroxides, for the D-line at 17·5°, according to B. Wagner,[43] are:

	2	4	6	8	10	15	20 per cent.
NaOH .	1·33866	1·34388	1·3477	1·35334	1·35755	1·36773	—
KOH .	1·33719	1·34101	1·34465	1·34803	1·35151	1·35921	1·36658

E. Briner's formula for the index of refraction μ for the D-line for sodium hydroxide of conc. w grms. per litre, is $\mu=1·3334+0·0002694w-0·000000289w^2$; and for potassium hydroxide, $\mu=1·3342+0·0001866w-0·000000112w^2$.

In 1801, H. Davy stated that[44] "dry caustic potash and soda are conductors of galvanism when rendered fluid by a high degree of heat," but the fact made little impression, for, about ten years later, he said that water is necessary for these substances to conduct electricity. M. Faraday made observations on the electrical conductivity of fused potassium hydroxide. The **electrical conductivities** of aq. soln. of the alkali hydroxides[45] are indicated in Table XII, where v denotes the

number of litres that contain a mol. of the hydroxide in soln. The electrical conductivity of a normal soln. of sodium hydroxide at 18° is 145×10^{-7}; and of potassium hydroxide, 170×10^{-7}. M. H. van Laer electrolyzed N-soln. of sodium hydroxide, and found the yield 17·5 per cent. of that indicated by Faraday's law; and is dependent on temp., hydrostatic press., diffusion, and electrical osmosis.

TABLE XII.—MOLECULAR ELECTRICAL CONDUCTIVITIES OF AQUEOUS SOLUTIONS OF THE ALKALI HYDROXIDES.

	F. Kohlrausch at 18°.					H. T. Calvert at 25°.			
v =	0·100	0·200	0·500	1·0	2·0	4·0	8	16	32
LiOH	—	80·0	105·4	125·3	138·8	189·1	198·3	204·7	208·9
NaOH	18·96	15·2	124·4	148·8	163·4	207·3	217·8	222·4	227·7
KOH	42·3	91·0	150·4	172·1	185·6	228·9	237·2	243·9	246·3
RbOH	—	—	—	—	—	240·0	242·3	249·1	250·9
CsOH	—	—	—	—	—	241·9	245·6	251·4	255·7

The specific electrical conductivity κ of sodium hydroxide[46] at a temp. $\theta°$ is $\kappa=\kappa_0(1+a\theta+b\theta^2)$, where κ_0, a, and b for 2·61 per cent. soln. are respectively 0·0256, 0·0298, and 0·000009; and for 42·7 per cent. soln. 0·0639, 0·0889, and 0·004467 respectively. For potassium hydroxide $\kappa=\kappa_0\{1+a(\theta-18)^2\}$, where $a=0·01936$ and $b=0·0000393$ for $v=0·001$; and $a=0·01901$ and $b=0·0000323$ for $v=0·01$. The **transport numbers** of the ions of lithium hydroxide have been measured by J. Kuschel;[47] of sodium hydroxide by G. Wiedemann, J. Kuschel, O. J. Lodge, and W. Bein; and of potassium hydroxide by J. F. Daniell, E. Bourgoin, G. Wiedemann, and B. D. Steele. J. Kuschel's results are for the cation of 0·201N-, 0·402N-, and 1·495N-soln. of LiOH, 0·848, 0·862, and 0·890 respectively; for 0·108N-, 0·285N-, and 1·084N-soln. of NaOH, 0·843, 0·800, and 0·827 respectively; and for 0·103N-, 0·190N-, and 0·804N-soln. of KOH, 0·742, 0·730, and 0·739 respectively.

The large ionic conc. of the hydroxylic ions in soln. of the alkali hydroxides is connected with their strong basic properties. This conclusion has been confirmed by measurements of the electrical conductivities, the effect on the velocity of hydrolysis of organic esters, and the heat of neutralization.[48] The **degree of ionization** of a soln. of sodium hydroxide containing 0·002 mol. per litre is 94·1 per cent.; 1·0 mol., 72·2 per cent.; for 0·00107 mol. of potassium hydroxide, 98·0 per cent.; and for 0·1109 mol. KOH, 82·3 per cent. According to S. Arrhenius, the **heat of ionization** of sodium hydroxide in $\frac{1}{10}N$-soln. is −1·292 Cals. at 35°. The **decomposition potential**[49] of a 2N-KOH soln. is 1·70 volt. The decomposition potential of molten sodium hydroxide at 390° on two points of the cathode is 1·16 and 2·06 volts—one refers to hydrogen, the other to sodium ions; at higher temp., the lower point is not so sharp. M. Chow calculated the **free energy** of potassium hydroxide in aq. soln. from the e.m.f. of cells of the type Hg|HgO, KOH|$K_{amalgam}$ with the alkali at different conc. and at 25°.

The **dielectric constant** of a 5 per cent. soln. of potassium hydroxide is 7·12.[50] Potassium hydroxide is **diamagnetic**[51]; its **magnetic susceptibility** is $-0·35\times10^{-6}$ at 22°.

As previously indicated, lithium hydroxide begins to decompose into the monoxide[52] when heated above its m.p., but the other hydroxides are not so readily decomposed, and although some decomposition does occur at a red heat, the monoxides of the other alkali metals cannot be obtained in this way. When *the hydroxides are heated in air some oxygen is absorbed, and the product then* furnishes reactions indicating that some peroxide has been formed.

The alkali hydroxides are strong bases, and they form neutral normal salts by reacting with the strong acids; the normal salts with the weak acids—*e.g.* carbonic,

boric, orthophosphoric, or silicic acid—have an *alkaline* reaction. According to R. Pictet,[53] conc. sulphuric acid does not attack the hydroxide at temp. below $-80°$. When alkali hydroxide is fused with most of the silicates, phosphates, or sulphates, a soluble alkali salt is formed, and hence fusion with potassium or sodium hydroxide (or carbonate) is a favourite method for opening up these insoluble compounds preparatory to analysis. The sodium hydroxide is usually preferred to the potassium compound because of the greater ease with which the sodium salts are subsequently washed from the precipitates. Soln. of the alkali hydroxides precipitate the hydroxides of most of the metals from soln. of their salts, and, with the exception of the hydroxides of the alkaline earths, these hydroxides are very sparingly soluble in water. The hydroxides of lead, antimony, tin, aluminium, chromium, and zinc are soluble in an excess of the reagent in virtue of the formation of soluble double oxides—*e.g.* $Pb(OK)_2$, potassium plumbite, etc. Soln. of the alkali hydroxides hydrolyze ethereal salts.

For the action of **ozone** on the alkali hydroxides, see the alkali tetroxides, and ozone. **Fluorine** reacts in the cold, forming the alkali fluoride, water, and ozonized oxygen. **Chlorine** reacts with sodium or potassium hydroxide in an analogous manner: $2Cl_2+4KOH+2H_2O+O_2$, but only at a red heat; in the cold, various oxychlorine compounds are formed. The reactions with **bromine** and **iodine** are similar. According to A. Reychler,[54] the reaction with **chlorine peroxide** corresponds cold with the equation $2ClO_2+2KOH=KClO_2+KClO_3+H_2O$. **Sulphur** gives with the alkali hydroxide—soln. or solid—a mixture of the sulphide and thiosulphate. The reaction between sulphur and the alkali lye is the more rapid the more conc. the soln.; a soln. with but 0·4 grm. of sodium hydroxide per litre is said not to be attacked either cold or hot; the solids combine by mere trituration in a mortar.[55] At the m.p., fused potassium hydroxide and sulphur form the pentasulphide and a sulphate. **Selenium** under similar conditions gives the selenide and selenite. **Nitric oxide** is gradually absorbed by potash lye, forming nitrous oxides and potassium nitrate. According to F. Emich, the reaction at 125° with anhydrous hydroxide corresponds with $4KOH+6NO=N_2+4KNO_2+2H_2O$. E. C. Franklin and C. A. Kraus found sodium hydroxide to be almost insoluble in liquid **ammonia.** M. Skossareswky and N. Tchitchinadzé[56] found that the sat. soln. between $-40°$ and $-45°$ contains between 1 and 4 parts of the compound per million of solvent. The presence of moisture has a great influence on the solubility. **Phosphorus** seems to produce a phosphide and oxyacid salts—phosphite, phosphate, and hypophosphate; but the phosphide is not stable in the presence of water and forms hydrogen phosphide. The regular method of preparing hydrogen phosphide is to boil phosphorus with the alkali lye. **Arsenic** behaves in an analogous manner, forming arsenic hydride and an alkali arsenite. **Phosphorus** disulphide gives complex compounds.[57] The alkali hydroxides are reduced when heated with **carbon,** and the metal is liberated along with hydrogen and carbon monoxide—according to A. A. B. Bussy,[58] some hydrocarbons are also formed. M. C. Boswell and J. V. Dickson have studied the oxidation of **carbon monoxide** by fused sodium hydroxide, which results in the formation of sodinm formate and oxalate; they have also studied the action of the fused hydroxide on **phenols** and **sulphonic acids.** Alkali formate is formed when the lye absorbs **carbon monoxide.** K. A. Hofmann said the reaction is active in the presence of copper; and, according to M. Berthelot and C. Matignon, the heat developed in converting potassinm hydroxide to the formate is 6·8 Cals. According to J. Kolb, and H. Debray, the dried oxides or hydroxides of sodium and potassium do not increase in weight in an atm. of dry **carbon dioxide,** but the moist alkalies absorb carbon dioxide with avidity. When amorphous **silicon** is heated to 100° with conc. potash lye, the alkali silicate and hydrogen are formed. Similar products are obtained when the alkali hydroxide is fused with **silicon.** **Zinc** acts in a similar manner: $Zn+2KOH=Zn(OK)_2+H_2$. **Calcium** displaces sodium when fused at a red heat with the hydroxide. When the hydroxide is fused with **silica** or **boric oxide,** a silicate or borate is formed

and water is evolved. Fused alkali hydroxides attack vessels of **silver, nickel,** and **gold**—silver and nickel resist the best. **Platinum** is attacked if air has access.

Fused sodium hydroxide is active in effecting many oxidations. E. Peligot [59] reported that **chromous hydroxide** is oxidized in the presence of aq. potassium hydroxide with the evolution of hydrogen, and G. Baugé obtained $2Cr_3O_4.3H_2O$ by the action of boiling water on **potassium chromous carbonate** when hydrogen and carbon dioxide are evolved; A. Wurtz found that **hypophosphites** with boiling aq. alkali hydroxides form phosphates and hydrogen; W. Muthmann and W. Nagel similarly converted **molybdenum dichloride** into trihydroxide. M. C. Boswell and J. V. Dickson oxidized **sodium arsenite** and **ferrous sulphate** by fused sodium hydroxide; hydrogen was simultaneously evolved. Much hydrogen was also evolved with **stannous chloride** and **vanadium sulphate,** less with **cerous sulphate,** and still less with **uranous sulphate.** Neither **sodium nitrite** nor **sodium sulphite** was oxidized; this is remarkable in view of the ready oxidation of these salts in aq. soln. The mechanism of these reactions consists ultimately in the decomposition of water, the oxygen carrying the oxygen acceptor to a higher stage of oxidation and the hydrogen being evolved in the gaseous state. Reactions with fused or dissolved alkali hydroxides are described in the literature in which the other reacting compound acts as both an oxygen and hydrogen acceptor, one mol. being oxidized and one mol. simultaneously reduced. In such cases the hydrogen, instead of being evolved in the free state, goes to reduce a second mol. These are in all probability special cases of the general oxidizing action of alkali hydroxides, with probably the same mechanism involving the decomposition of water. The following are instances of this action: A. Ditte observed that stannous hydroxide reacts with very strong soln. of potassium hydroxide at ordinary temp. with the formation of tin and potassium stannate; also C. F. Rammelsberg observed that the lower phosphorus oxy-salts, such as $NaH_2PO_2.H_2O$, when heated, pass into phosphates and phosphine. The evolution of hydrogen when many metals as aluminium, zinc, and lead are boiled with sodium hydroxide soln. is no doubt initiated by this general oxidizing action of water catalyzed by sodium hydroxide, $Zn+2H_2O=Zn(OH)_2+H_2$.

Uses of the alkali hydroxides.—A soln. of potassium hydroxide is used in the laboratory as an absorbent for carbon dioxide, the sodium componnd is not so often used because of the formation of less soluble sodium carbonate which is liable to choke the delivery tubes with crystals. Potassium hydroxide is used in making soft soaps; the corresponding sodium compound gives the ordinary hard soaps. The hydroxide fused with a little lime is used as a cautery—*pierre à cautère*. The alkali lye is also used as a cleansing fluid, since it forms soluble soaps with many greases and fats. The lye also dissolves animal tissues.

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§ 12. The Alkali Fluorides

The complex fluorides are in many ways closely analogous with the complex salts of the *other halogens, but, owing to the peculiarity of the alkali fluorides in uniting in a bimolecular form with the metal fluorides, a new factor comes into consideration, and this introduces* so many complications that the likeness appears less than it really is.—P. PFEIFFER (1902).

Sodium fluoride occurs in combination with some minerals—*e.g.* cryolite—and the fluorine in many natural waters is probably combined as sodium fluoride. *All the five alkali metals form normal* fluorides of the type RF; and acid fluorides RF.HF, or still higher acid fluorides RF.*n*HF are known.

The preparation of the alkali fluorides.—The normal fluorides, RF, are formed when the metals are exposed to the action of fluorine or hydrogen fluoride gas,[1] and also when the alkali metal is exposed to the vapour of boron trifluoride, silicon tetrafluoride, and other metal fluorides. These modes of formation are not suitable for the preparation of the alkali fluorides. J. L. Gay Lussac and L. J. Thénard[2] prepared potassium fluoride in 1811, and J. J. Berzelius, lithium fluoride in 1824, *by treating the hydroxide or carbonate with hydrofluoric acid in a platinum dish.* It may be necessary to filter off a little fluosilicate derived from the hydrofluosilicic acid present in the hydrofluoric acid as an impurity. The soln. is evaporated to dryness and calcined. This product always has an alkaline reaction, presumably because the fluoride is slightly hydrolyzed: $KF+H_2O=KOH+HF$. According to M. Guntz,[3] it is best to make the normal fluoride by calcining the acid fluoride KF.HF. The residue is then quite neutral to the usual indicators. This method of preparation is particularly applicable to lithium fluoride. C. Chabrié recommends *heating the acid fluoride of cæsium or rubidium with ammonium fluoride in* order to make the normal fluoride, CsF, or RbF. J. J. Berzelius[4] made sodium fluoride by boiling a conc. aq. soln. of sodium fluosilicate, Na_2SiF_6, with sodium carbonate; evaporating the soln. until it became opalescent through the separation of silica; decanting off the mother liquor; and evaporating the soln. to dryness. The mass was then mixed with ammonium carbonate; calcined; and finally crystallized from aq. soln.

J. Reich[5] also patented a process based on the calcination of the alkali fluosilicate or fluoborate with an oxide of the alkaline earths. When the calcined mass is lixiviated with water, the alkali fluoride is obtained in soln. L. Schuch[6] made sodium fluoride by boiling finely powdered cryolite with a conc. soln. of sodium hydroxide—the alumina and silica pass into soln.—sodium fluoride crystallizes from the cooling soln. Sodium silicate can be used in place of the hydroxide. F. Jean made sodium fluoride by leaching a calcined mixture of fluorspar, limestone, Glauber's salt, and charcoal.

If the soln. of the potassium salt be evaporated above 40°, anhydrous cubic crystals, KF, are obtained, but below this temp., long prismatic crystals of the **dihydrate of potassium fluoride,** $KF.2H_2O$. The hydrate is also obtained by evaporating a soln. of potassium fluoride in vacuo; or by precipitation from the aq. soln. by the addition of alcohol.[7] At temp. below 20°, a **tetrahydrate of potassium fluoride,** $KF.4H_2O$, melting at 19·3°, is formed. Rubidium fluoride forms two *hydrates,* $2RbF.3H_2O$ and $3RbF.H_2O$; and cæsium fluoride the hydrates $2CsF.3H_2O$ and $3CsF.2H_2O$.

Properties of the alkali fluorides.—The anhydrous alkali fluorides crystallize in the cubic system.[8] Lithium fluoride forms regular octohedrons and nacreous plates; sodium fluoride crystallizes in cubes, but in presence of sodium carbonate, the crystals are octohedrons. The cubic crystals are frequently *en tremies*. H. Schwendenwein has discussed the **space lattice** of the alkali fluorides, and K. Fajans and H. Grimm estimated the distance of the atoms apart in sodium and potassium fluorides to be respectively $2·34\times10^{-8}$ and $2·67\times10^{-8}$ cm.; and the respective lattice energies to be 210·4 and 192·2 Cals. per mol. The taste of potassium fluoride is acrid and salty.

The **specific gravities** of the fluorides are: lithium fluoride,[9] 2·5364 to 2·612—F. W. Clarke gives 2·295 at 21·5°; sodium fluoride, 2·558 at 41°, according to F. W. Clarke, and 2·766 according to H. C. F. Schroeder; potassium fluoride, 2·096 at 21·7°. K. Fajans and H. Grimm have investigated the mol. vol. of the alkali fluorides; they estimate the mol. vol. of rubidium and cæsium fluoride to be respectively 28·8 and 29·1 c.c. at 25°. J. M. Jäger's values for the sp. gr., the **surface tension** (ergs per cm.), and **molecular surface energy** (ergs per sq. cm.) of the molten fluorides are indicated in Table XIII.

TABLE XIII.—THE SPECIFIC GRAVITIES AND SURFACE TENSIONS OF THE MOLTEN ALKALI FLUORIDES.

	Temp.	Surface tension.	Sp. gr.	Mol. surface energy.	Temp. coeff. per degree.
LiF	868·5°	249·5	1·789	1485·4	0·40
	1270°	201·1	1·599	1290·4	0·70
NaF	1010°	199·5	1·936	1551·8	0·52
	1546°	143·5	1·634	1249·8	0·52
KF	912·7°	138·4	1·869	1368·1	0·33
	1310°	104·9	1·604	1148·4	0·83
RbF	802·6°	127·2	2·894	1389·2	1·13
	1085·4°	102·2	2·605	1197·2	0·40
CsF	722·5°	104·5	3·583	1270·0	0·72
	1100°	78·9	3·117	1052·3	0·36

J. M. Jäger gives for the sp. gr. D of molten lithium fluoride at $\theta°$ (water at 4° unity), $D=1·798-0·0004375(\theta-850)$; sodium fluoride $D=1·942-0·000564(\theta-1000)$; potassium fluoride $D=1·878-0·000669(\theta-900)$; rubidium fluoride $D=2·873-0·000967(\theta-825)-0·000000247(\theta-825)^2$; and for cæsium fluoride, $D=3·611-0·001234(\theta-700)$.

When pure and dry, potassium fluoride can be kept in glass vessels, but if moisture be present, the glass is etched. Soln. of the fluoride also etch glass and porcelain, and some silica is dissolved.[10] According to T. H. Norton and D. M. Roth,[11] potassium fluoride volatilizes in the hottest part of the Bunsen flame about three times as fast as the same amount of the chloride; and sodium fluoride about eight times as fast as the corresponding chloride; and S. Waldbott found that about half a gram of sodium fluoride lost 0·4 per cent. when heated 6 min. over the Bunsen flame—the residue had an alkaline reaction, showing a slight decomposition had taken place. According to C. Poulenc,[12] lithium fluoride is partially volatilized when heated to 1100° or 1200° in a stream of hydrogen fluoride. The **melting points** which have been reported are not very concordant. Many determinations have been made on more or less impure samples, and more care seems to have been taken in eliminating errors in the temp. determinations than in purifying the salts. E. Hintz and H. Weber [13] reported a sample of commercial salt to contain 65·65 per cent. of sodium fluoride and 3·97 per cent. of water. The remaining impurity contained: NaCl, 0·74; Na_2CO_3, 13·89; Na_2SO_4, 1·96; K_2SO_4, 0·74; $CaCO_3$, 0·25; $MgCO_3$, 0·32: Fe_2O_3, 0·48; Al_2O_3, 0·17; Na_2O (as silicate), 1·50; SiO_2 (partly as sodium silicate), 10·11 per cent. T. Carnelley [14] gives 753° ± 9° for the m.p. of rubidium fluoride; and O. Ruff and W. Plato give 855° for potassium fluoride; but numbers ranging from 867° to 837° have been given for the f.p. of potassium fluoride. G. Scarpa gives 857°; W. Plato, 859·9°; B. Karandéeff, 867°; N. S. Kurnakoff and S. F. Schemtschuschny, 837°; N. A. Puschin and A. V. Bascoff, 885°. Similarly for sodium fluoride the numbers vary from 980° to 997°—N. A. Puschin and A. V. Baskoff give 1040°; N. S. Kurnakoff and S. F. Schemtschuschny, 997°; O. Ruff and W. Plato, 980°; G. Scarpa, 1005°; and W. Plato, 992°. For lithium fluoride T. Carnelley gives 801° ± 15°, and

G. Scarpa, 840°. According to N. A. Puschin and A. V. Baskoff, the best representative values are:

	LiF	NaF	KF	RbF	CsF
M.p.	870°	1040°	885°	833°	715°

The f.p. curves of several binary systems have been worked out; thus, with potassium chloride and fluoride, W. Plato[15] obtained the typical **V**-curve with a eutectic at 605° corresponding with 61 mols. per cent. of KCl; with potassium fluoride and bromide the eutectic melts at 610°, when 77 per cent. of the bromide is present; and with potassium fluoride and iodide, the eutectic melts at 580° when 87 per cent. of the iodide is present; with sodium chloride and fluoride, the eutectic is at 675°, corresponding with 72·5 mols. per cent. of NaCl. Mixtures of sodium and potassium fluorides also have a eutectic at 700°, corresponding with 60 mols. per cent. of KF. With potassium sulphate and fluoride, B. Karandéeff obtained two eutectics: one at 883°, corresponding with 41 mols. per cent. of the sulphate; and the other at 788°, corresponding with 83 mols. per cent. The intervening maximum corresponds *with the compound* $K_2SO_4.KF$, *which melts at* 887°, *and decomposes at* temp. below 578°. With sodium fluoride and sulphate, A. Wolters found two eutectics at 773° and 742° respectively, corresponding with 40 and 70 mols. per cent. of Na_2SO_4; the intervening maximum melts at 781°, corresponds with $Na_2SO_4.NaF$. Sodium fluoride has an enantiomorphic transition point at 105°. J. C. G. de Marignac prepared hexagonal crystals of the double salt $NaF.Na_2SO_4$ by crystallization from sulphuric acid sat. with hydrogen fluoride. It can be recrystallized from water without decomposition. A. Wolters also studied the ternary system $NaCl—NaF—Na_2SO_4$. The transformation points of sodium and potassium hydroxides are lowered by the corresponding fluorides. G. Scarpa found the binary mixtures of lithium fluoride and hydroxide; sodium fluoride and hydroxide; and of potassium fluoride and hydroxide gave two solid soln. with a miscibility break.

According to E. Baud, the **specific heat** of sodium fluoride[16] between 15° and 53° is 0·2675; and according to J. N. Brönsted, between 0° and 20°.

	LiF	NaF	KF	RbF	CsF
Sp. ht.	0·3725	0·2610	0·1997	0·1153	0·0796
Mol. ht.	9·66	10·96	11·60	12·04	12·09

F. Koref found the sp. ht. and mol. ht. of sodium fluoride between —191·0° and —82·5° to be respectively 0·1740 and 7·31; and between 0° and —75·2°, 0·2483 and 10·43. Similarly, for potassium fluoride between —191·6 and —81·8°, 0·1559 and 9·06; and between 0° and —76·4°, 0·1930 and 11·21. According to W. Plato,[17] *the* **heats of fusion** *of sodium fluoride is 186·1 cals., and of potassium fluoride,* 108·0 cals. per gram. G. Bartha found potassium fluoride volatilized rapidly in vacuo at 910°. The **heat of formation** of lithium fluoride is Li+F+aq.=LiFaq. +115·8 Cals.; with sodium fluoride: $Na_{solid}+F_{gas}=NaF_{solid}+109·3$ Cals.; and with potassium fluoride, 115·2 Cals. A. Guntz gives 110·6 Cals. The heats of formation of the alkali fluorides from solid hydrogen fluoride are NaF, 8·3 Cals.; KF, 12·8 Cals.; RbF, 13·8 Cals.; and CsF, 14·77 Cals. The **heat of neutralization** of lithium fluoride, according to E. Petersen,[18] is HFaq.+LiOHaq.=LiFaq.+16·4 Cals.; the usual value for the heat of neutralization of an acid by a base is 13·7 Cals., and the deviation from this value by lithium fluoride supports the view that the polymer Li_2F_2 is formed. With sodium fluoride, the heat of neutralization is 16·27 Cals. The **heat of solution** of sodium fluoride is $NaF_{solid}+400H_2O$ is —0·6 Cal.; of anhydrous potassium fluoride, at 20°+3·6 Cals., and for the dihydrate —1·0 Cal. Hence the solubility of the anhydride must decrease with a rise of temp., that of the hydrate increase. The **heat of hydration,** $KF+2H_2O=KF.2H_2O+4·6$ Cals.

The **solubility** of the alkali fluorides increases in a marked way in passing from

the lithium to the potassium salt. According to F. Mylius and R. Funk,[19] 100 grms. of water dissolve 0·27 grm. of lithium fluoride at 18°. The low solubility of lithium fluoride is supposed to support the assumption that the salt is present as Li_2F_2,—a salt of the dibasic H_2F_2. The salt is still less soluble in the presence of ammonium fluoride, or ammonia—according to A. Carnot, one part of lithium fluoride is then soluble in 3400 of the reagent. With sodium fluoride there is a eutectic at —5·6°; and at 15°, a sat. soln. contains 3·85 per cent. of the anhydrous salt, and at 18°, 4·22 per cent. A. Ditte found that at 21°, the solubility of sodium fluoride in *hydrofluoric acid* first decreases to a minimum and then increases with increasing conc. of the acid, such that 100 grms. of water have in grams:

HF	0	1·00	4·58	5·65	8·38	12·97	59·64	77·74
NaF	4·17	4·14	2·25	2·27	2·29	2·38	4·88	8·17

Similarly, with potassium fluoride in hydrofluoric acid:

HF	0	1·21	3·73	6·05	12·50	20·68	74·20	119·20
KF	96·3	72·0	40·4	30·4	30·5	38·4	105·0	169·5

the minimum correspond with a soln. containing 11·36 grms. of HF and 29·6 grms. of KF. Potassium hydrogen fluoride is formed which increases with the conc. of the acid, and with the proportions of normal fluoride in accord with the mass law.[20] F. Mylius and R. Funk found 100 grms. of water dissolve 92·3 grms. of potassium fluoride at 18°, for 100 grms. of the sat. soln. contain 48 grms. of KF, and the sp. gr. of the soln. is 1·502. According to H. Rose, below 40°, the solid phase is the dihydrate, $KF.2H_2O$; above 40°, the anhydrous salt. Potassium fluoride is very sparingly soluble in *alcohol*; it dissolves in aq. alcohol, and in conc. soln. of *potassium acetate*.

The **specific gravity of a solution** of lithium fluoride, sat. at 18°, is 1·003. The sp. gr. of soln. of sodium fluoride, according to G. T. Gerlach, are for a 1·11 per cent. soln. at 15° (water at 15° unity), 1·0110; a 2·22 per cent. soln., 1·0221; and a 3·32 per cent. soln., 1·0333. The sp. gr. of aq. soln. of potassium fluoride determined by F. Kohlrausch, at 18° (water at 4° unity):

KF	6·91	12·24	22·51	33·58	39·97
Sp. gr. . . .	1·0575	1·1025	1·2000	1·3070	1·3780

G. Tammann[21] has determined the **lowering of the vapour tension** of water, by the addition of x grms. of the salt to 100 grms. of water at 100°, in mm. of mercury:

NaF	2·48	4·46	4·56	—	—	—	—	—
KF	—	—	—	4·71	9·98	34·26	42·17	54·76
Lowering . . .	13·9	24·4	25·1	17·8	41·8	164·1	206·9	274·0

The **partial pressure of ammonia** and water at 25° is 13·45 mm.; in $\frac{1}{2}N$-soln. of potassium fluoride 16·04; in N-KF, 18·65; and in 1·5N-KF soln. 21·47 mm.[22] The partial press. of the ammonia is therefore raised proportionally with the conc. of the salt, where it would probably be lowered if the fluoride formed a complex with ammonia. According to W. Biltz,[23] the **freezing point** of a soln. containing 0·3379 grm of potassium fluoride per 100 grms. of water, 0·202°; and with 1·031 grm. of salt per 100 grms. of water, 0·595; and with 5·445 grms. of salt, 3·168°. The depression of the f.p. of rubidium fluoride was measured by H. Eggeling and J. Meyer. With 16 of water and 0·2005 grm. of salt, the f.p. was depressed 0·414°; with 36 of water and 0·0024 grm. of salt, 0·906°. The corresponding mol. wt. are 55·7 and 56·8. The theoretical value for RbF is 104. Hence, the normal rubidium fluoride in aq. soln. is probably bimolecular, and almost completely ionized: $RbF = Rb^{\cdot} + F'$ in dil. soln. This also is the case with potassium fluoride.

The mol. **electrical conductivity** of a soln. of potassium fluoride at infinite

dilution is 111·35; and of sodium fluoride 90·15. The mol. conductivities λ at 18° for soln. containing n mols. of the salt per litre, when the degree of ionization is α:

n	0·0001	0·001	0·01	0·1	0·2	0·5	1·0
NaF λ . .	89·35	87·86	83·48	73·14	68·0	60·0	51·9
NaF α . .	99·1	97·5	92·6	81·1	75·4	66·6	57·6
KF λ . .	110·47	108·89	104·28	94·02	—	82·6	76·0
KF α . .	99·2	97·8	93·7	84·4	—	74·2	68·3

S. Arrhenius[24] estimates the temp. coeff. of the conductivity of sodium fluoride between 18° and 40° to be about 0·0253 per degree; and the heat of ionization of sodium fluoride to be 0·084 Cal. F. M. Jäger and B. Kampa measured the mol. conductivity, μ, of potassium fluoride at $\theta°$ between 863° and 975°, and found $\mu=101·8+0·3163(\theta-900)$. According to A. Heydweiller, the **dielectric constants** of powdered and compact sodium fluoride are respectively 2·09 and 3·94; and for potassium fluoride 2·82 and 5·92.

The stability of the alkali fluorides increases in passing from sodium to cæsium. Lithium fluoride is scarcely attacked by water vapour at a red heat. Potassium fluoride is very deliquescent. H. Pauli[25] could detect no hypofluorites or fluorates when aq. soln. of potassium fluoride were electrolyzed; but much ozone was formed. The alkali fluorides are decomposed by cold conc. sulphuric acid and also by chlorine. If a stream of dry hydrogen chloride is passed over potassium fluoride[26] at ordinary temp., potassium chloride, and potassium hydrogen fluoride are formed; if heated, the latter is decomposed into the normal fluoride and hydrogen fluoride; the normal fluoride is again attacked, and the same sequence of changes continues until all is converted into the chloride. If in soln., the base divides itself between the two acids. The alkali fluorides are decomposed by many organic acids—*e.g.* acetic, formic, tartaric, malic, lactic, benzoic, and salicylic acid—with the liberation of hydrofluoric acid. Carbon dioxide bubbled through the soln. acts in a similar way.[27] The alkali fluorides are not attacked by oxygen hot or cold. When heated with ammonium chloride, the alkali chloride is formed.[28] They are not decomposed by silica if heated below the m.p. of the salt, since by leaching with water, the silica can be recovered unchanged. An excess of limewater, or magnesia, precipitates calcium fluoride from soln. of the alkali fluorides.[29] Sodium fluoride is a valuable preservative for wood, and can be used with advantage in place of zinc chloride (*q.v.*), and would probably displace the latter if the costs of production could be reduced.

The acid fluorides.—J. J. Berzelius[30] obtained small crystals of a **lithium hydrofluoride,** presumably LiF.HF, from a soln. of the normal fluoride in hydrofluoric acid; the acid salt is more soluble in water than the normal fluoride. An analogous **sodium hydrofluoride,** NaF.HF, was also discovered by J. J. Berzelius. It is made by dissolving the normal fluoride in hydrofluoric or acetic acid.[31] It forms rhombohedral or trigonal crystals which, according to H. Rose, are isomorphous with the corresponding salt of potassium. The acid salt is converted into the normal salt by heat, and it is broken down into the normal salt and hydrofluoric acid when dissolved in water,[32] in which it is but sparingly soluble. It is more soluble in hot than in cold water. Its heat of formation[33] is 17·1 Cals.; and its heat of soln., at 12°, is $NaF.HF+400H_2O=-6·62$ Cals. The mono-acid salt, **potassium hydrofluoride,** KF.HF, was made by J. J. Berzelius as described above; it is sometimes called **Frémy's salt** in honour of E. Frémy's *Recherches sur les fluorures* (1854). E. Frémy[34] prepared the salt by pouring a conc. soln. of hydrofluoric acid into a similar neutral soln. of the fluoride produced by saturating hydrofluoric acid with potassium carbonate. Crystals of sparingly soluble acid fluoride immediately separate from the soln. They contain a little potassium fluosilicate which can be separated by several recrystallizations. The acid fluoride is dried first between folds of unsized filter paper, then in vacuo, and finally in a drying oven. While the neutral fluoride is deliquescent, the acid fluoride is not so. H. Moissan prepared

the acid fluoride for making anhydrous hydrogen fluoride, in the following manner:

A given volume of hydrofluoric acid, freed from silica, was divided into two equal portions, and one portion was exactly neutralized by purified potassium carbonate. The two portions were mixed, and thus converted into the acid fluoride. The salt itself was obtained by evaporating the soln. in a platinum basin, on a water-bath, at 100°; and completely dried under reduced press. (say 20 mm.) over conc. sulphuric acid. Two or three sticks of caustic potash were exposed in the same evacuated vessel. The salt was powdered from time to time in an iron mortar so as to expose fresh surfaces. The sulphuric acid and potash were renewed every 24 hrs. for about 15 days.

A. P. Borodine prepared this salt in rectangular plates (cubic system) by evaporating the normal fluoride with acetic or alcoholic benzoic acid. By slow evaporation, cubic crystals, some *en trèmies*, are formed. According to H. de Sénarmont,[35] the crystals are tetragonal. The heat of soln. of the mono-acid salt is $KF.HF+400H_2O=6·0$ Cals. The dry salt melts when heated, and gives off anhydrous hydrogen fluoride. It dissolves readily in water, but sparingly in hydrofluoric acid; it is readily soluble in a conc. soln. of potassium acetate. It is precipitated from soln. by alcohol, though it dissolves in dil. alcohol. When an intimate mixture of this salt with a powdered silicate is heated, the mineral is decomposed, and most of the silicon is evolved as silicon fluoride. According to H. Moissan,[36] if a soln. of 5·6 grms. of the mono-acid salt in 10 grms. of hydrofluoric acid be cooled to $-23°$, crystals of the tri-acid salt—**potassium trihydrofluoride**—KF.3HF, are formed; and the same salt is produced by evaporating a soln. of one mol. of potassium fluoride with three mols. of hydrofluoric acid on an oil bath at 85°, the clear liquid which remains when no more acid fumes are evolved freezes to a hard crystalline mass at 65°. It does not lose acid in dry air or in vacuum. It dissolves in water with strong cooling, and it decomposes into the mono-acid and hydrofluoric acid. It melts at 100°, and with a stronger heating, it decomposes. The salt reacts vigorously with sulphuric acid, aqua ammonia, and potash-lye. The corresponding di-acid salt—**potassium dihydrofluoride**—KF.2HF, is made in an analogous manner. It melts at 105°, and its properties are analogous with the tri-acid salt. The heats of formation are: $KF_{liq.}+HF_{liq.}=KF.HF_{liq.}-0·33$ Cal.; $KF_{solid}+HF_{liq.}=KF.HF+13·9$ Cals.; $KF.HF+HF_{liq.}=KF.2HF+6·5$ Cals.; $KF.2HF+HF_{liq.}=KF.3HF+5·1$ Cals.; $KF.HF+2HF_{liq.}=KF.3HF+11·6$ Cals.; $KF+2HF_{gas}=KF·2HF+35·2$ Cals.; and $KF+3HF_{gas}=KF.3HF+47·1$ Cals. H. Eggeling and J. Meyer[37] have prepared the corresponding acid fluorides of rubidium—**rubidium, mono-, di-, and tri-hydrofluorides**—and they were found to resemble the corresponding potassium salts. C. Chabrié[38] has prepared **cæsium hydrofluoride,** CsF.HF, in a similar manner to the process employed for the corresponding potassium salt, and the properties are analogous. The higher acid fluorides of cæsium—CsF.2HF and CsF.3HF—have also been prepared. Metal salts corresponding with $HLiF_2$, $HNaF_2$, HKF_2, $HRbF_2$, and $HCsF_2$, and with potassium, rubidium, and cæsium salts of the di- and trihydrogen fluorides, have been reported. The stability of the alkali monohydrogen fluorides decreases in passing from sodium to cæsium; the contrary is the case with the normal fluorides.

According to S. Tanatar,[39] **potassium fluoride hydroperoxide,** $KF.H_2O_2$, is obtained by evaporating at 50° a soln. of one mol. of potassium fluoride in 2 mols. of 15 per cent. hydrogen peroxide, acidified with a few drops of hydrofluoric acid, so long as it does not decompose with effervescence. The cold soln. is treated with alcohol, and the denser layer is separated and evaporated in vacuo. Monoclinic acicular crystals of the salt $KF.H_2O_2$ are formed. They are stable at 70°, but slowly decompose at 110°. The crystals are readily soluble, and the mol. depression of the f.p., and the partition between ether and water, led S. Tanatar to believe that it is an addition product.

Monoclinic crystals of **potassium fluosulphate,** $K_3HS_2O_7F_2.H_2O$, have been

obtained by evaporating soln. of potassium sulphate or bisulphate in 40 per cent. acid. The corresponding rubidium and cæsium salts have been prepared. The **fluoselenates** *of these same elements—e.g.* $K_3HSe_2O_7F_2.H_2O$*—were also made in a similar* manner. The **oxyfluoiodates** are prepared in a similar manner from the alkali iodate and hydrofluoric acid, or the fluoride and iodic acid. The potassium salt, KIO_2F_2, *crystallizes in the rhombic system. Sodium, ammonium, rubidium, and* cæsium salts have also been made. A. Werner[40] represents the constitution of the oxyfluo-iodates by $[O_2IF_2]M$, where M denotes Na, K, Rb, Cs, or NH_4. He also regards the fluosulphates, fluodithionates, and the fluophosphates as addition products. Crystals—possibly triclinic—of **potassium fluodithionate,** $K_2S_2O_5F_2.2H_2O$, separate on cooling a warm sat. soln. of potassium dithionate in 40 to 60 per cent. hydrofluoric acid.[41] The rubidium salt has the composition $Rb_2S_2O_5F_2.3H_2O$, and the cæsium salt, $Cs_2S_2O_5(OH)F.H_2O$, is more stable than the corresponding potassium or rubidium salt. Many double salts with boron trifluoride, antimony trifluoride, silicon tetrafluoride, tin tetrafluoride have been reported.[42] The minerals cryolite, $AlF_3.3NaF$; pachnolite, $AlF_3.CeF_2.NaF$; and chiolite, $3AlF_3.5NaF$, are either double fluoride of aluminium and sodium[43] or solid soln. containing this compound. There are also the fluo-oxyniobates, fluomanganites, etc.

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§ 13. Ammonium Fluoride

Ammonium fluoride was made by H. Davy [1] by the action of ammonia gas on hydrogen fluoride—liquid or gas—and he demonstrated that no water is produced by the reaction. J. C. G. de Marignac obtained hexagonal plates or prisms of the salt by saturating a soln. of hydrofluoric acid with ammonia, and evaporating the soln. over caustic lime. W. Mills patented a process in which an intimate mixture of ammonium sulphate and calcium fluoride is heated. The ammonium fluoride formed by double decomposition is collected as a sublimate. J. J. Berzelius obtained the salt from ammonium chloride by heating an intimate mixture of ammonium chloride with just over twice its weight of sodium fluoride whereby a sublimate of ammonium fluoride free from the chloride is formed : $NH_4Cl+NaF=NaCl+NH_4F$. P. T. Austen and F. A. Wilber prepared ammonium fluoride for silicate analyses by treating hydrofluoric acid in a platinum dish with an excess of conc. ammonia and filtering the liquid through a filter paper previously washed with hydrofluoric acid, and supported in a ring of platinum wire, directly into a platinum crucible containing the silicate to be acted upon by the acid.

The properties of ammonium fluoride.—According to J. C. G. de Marignac, the crystals are too deliquescent for crystallographic measurements. B. Gossner [2] likewise obtained hexagonal uniaxial prisms or plates by crystallization from methyl alcohol. J. J. Berzelius says the crystals are stable in air. When differences of opinion exist as to the deliquescence or otherwise of the crystals of a salt in air, it

is probable that air in different hygrometric states has been under observation. J. J. Berzelius also says that when heated the salt fuses before an appreciable quantity sublimes; and that the sublimation occurs at a lower temp. than is the case with ammonium chloride. No reports are available as to whether the vapour of ammonium fluoride is dissociated like that of ammonium chloride. According to A. Gruntz,[3] the heat of formation $NH_{3aq.}+HF_{aq.}=NH_4F_{aq.}+15.2$ Cals; $NH_{3gas}+HF_{gas}=NH_4F_{solid}+37.3$ Cals.; and the mol. ht. of soln. is -1.5 Cals. J. H. and G. Gladstone found the mol. refraction for sodium light to be $M(\mu-1)/D=10.97$ for the salt in aq. soln. O. Reinkober studied the reflexion spectra of ammonium fluoride for ultra-red rays. The salt is easily soluble in water, and it is also soluble in methyl and ethyl alcohol. G. Carrara[4] has measured the solubility and electrical conductivity in methyl alcohol. H. N. Warren stated that an oily explosive liquid—nitrogen fluoride—accumulates about the anode during the electrolysis of an aq. soln. of ammonium fluoride, but O. Ruff and E. Geisel could not confirm this observation, and assume that H. N. Warren's ammonium fluoride must have contained some chloride. When a sat. aq. soln. of ammonium fluoride is electrolyzed in a glass U-tube with platinum electrodes (10 volts), hydrogen alone is given off at the cathode, and a mixture of nitrogen and oxygen at the anode, some fluosilicate is formed by the action of hydrofluoric acid on the glass. With a leaden tube, hydrogen is still given off at the cathode, but at the anode no nitrogen but only hydrogen and oxygen—never fluorine. However, the electrolysis of a soln. of ammonium fluoride in liquid hydrogen does furnish fluorine gas. According to O. Ruff and E. Geisel, ammonium fluoride is insoluble in liquid ammonia; and, according to J. J. Berzelius, this salt readily absorbs ammonia gas which on sublimation is expelled. J. J. Berzelius suggested that a basic salt is formed—the product is possibly ammonium ammino-fluoride, $NH_4F(NH_3)_n$, analogous to the ammino-compounds of the other ammonium halides, but J. Kendall and J. G. Davidson could not make an *ammonium ammino-fluoride*.

According to H. Rose,[5] quartz and boric oxide are converted into fluorides and volatilized when admixtures with ammonium fluoride are heated; one or more repetitions may be required for the complete volatilization of the silica. Nothing is lost when alumina, beryllia, ferric oxide, zirconia, chromic oxide, or tungstic oxide is similarly treated; potassium sulphate, or chloride, is not decomposed by this treatment; sodium phosphate, arsenite, or sulphate is but partially decomposed; while tantalum and columbium oxides are completely converted into volatile fluorides. J. J. Berzelius found that dry ammonium fluoride attacks glass in the cold, and, according to J. Davy, ammonia, and ammonium fluosilicate, $(NH_4)_2SiF_6$, are formed in the reaction; hence the use of ammonium fluoride for etching glass. H. Will says that 0.5 to 10 per cent. soln. of the salt do not attack guttapercha, and the soln. can be kept in platinum, silver, or guttapercha vessels.

Ammonium acid fluoride, or ammonium hydrofluoride, $(NH_4)HF_2$, or $NH_4F.HF$—J. C. Wiegleb[6] found aq. soln. of ammonium fluoride gives off ammonia gas slowly at ordinary temp., more rapidly when heated, and ammonium hydrofluoride, $(NH_4)HF_2$, is formed; there is a hydrolytic reaction: $2NH_4F_{aq}\rightleftharpoons NH_3+(NH_4)HF_2$. In moist air also the solid salt is readily transformed into the acid salt. J. J. Berzelius, indeed, prepared ammonium hydrofluoride crystals by evaporating a soln. of the neutral salt at 36°–40°, ammonia gas is at the same time evolved. H. Rose[7] made it by saturating commercial hydrofluoric acid with ammonia, and precipitated any impurities which might be present by treatment with ammonium sulphide and carbonate. After settling in glass vessels, the clear liquid was evaporated to dryness on a water-bath.

According to J. C. G. de Marignac and B. Gossner,[8] ammonium hydrofluoride forms rhombic crystals with axial ratios $a:b:c=0.9710:1:0.8626$, and A. des Cloizeaux found crystals which were optically uniaxial approximating to the tetragonal system; hence, says P. Groth, this salt probably exists in two polymorphic forms. B. Gossner gives the sp. gr. 1.503, and C. H. D. Bödecker,

1·211 (12°). According to H. Rose, the dry crystals are not deliquescent; J. J. Berzelius says they are. The crystals have a negative double refraction. Ammonium hydrofluoride volatilizes completely when heated. According to H. Rose, when ammonium hydrofluoride is mixed with silica or a silicate and calcined, the silicate is more readily decomposed than if hydrofluoric acid had been used. On electrolysis with a current of 5 ampères, O. Ruff and E. Geisel[9] obtained fluorine.

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§ 14. The Alkali Chlorides

Thou shalt offer salt with all thy meat offerings.—LEVITICUS.

Sodium chloride, commonly called salt, has been used in seasoning food from very ancient times. There is some doubt if the term was known to the Aryans before the linguistic separation. Isodorus, a writer near the beginning of the seventh century, *said that the word salam is derived from sol because it is obtained* by the action of the sun on sea water; others have supposed the word *salt* to be derived from *exilire*, to crackle and spring about, because common salt decrepitates when heated. Salt is frequently mentioned in the Bible, and the Jewish rites as well as those of almost all other nations, testify to the high esteem and sanctity with which the ancients regarded salt. The modern Arabians are said still to practise the *covenant of salt*, but only on occasions of the highest importance. The superstitious custom of throwing a pinch of salt over the shoulder in order to propitiate the fairies is probably the survival of an old superstition when salt was always included among the offerings to the gods. The Roman historian Pliny writes on salt in his *Naturalis historia* (**31**. 41). He says:

> The higher enjoyments of life could not exist without the use of salt. So necessary is this substance to mankind that even the pleasures of the mind can be expressed by no better term than the word salt—a name given to all effusion of wit. All the amenities of life—supreme hilarity and relaxation from toil—cannot be characterized better than the salt of life. Even in the very honours bestowed upon successful warfare, salt plays its part, and from it our word *salarium* is derived.

The term *salarium* or *salarium argentum*—salt money— was used by the Romans for the pay of generals and military tribunes, and hence followed the term " salary "; in some cases a man might " not be worth his salt."

Salt is considered to be an essential constituent of animal food; and it is said

that there are few things more distressing than *salt hunger*, and the dreaded *salt torture* of the Chinese provides the victim with ample food but no salt. One writer estimates that about 29 lbs. of salt per head of population per annum are used directly or indirectly with the food of man. The 0·1 per cent. of hydrochloric acid present in the gastric and mucous fluids of the alimentary canal is derived from the decomposition of salt taken with the food ; and it is estimated that a man requires between 16 and 17 lbs. of salt per annum merely for satisfying his normal physiological requirements. Plant-eating animals get much of the salt they require from grass and leaves, and they have been known to travel hundreds of miles to a *salt-lick*, or *salt-spring*, in order to satisfy their craving for salt. Carnivorous animals get their salt from the blood of the animals on which they feed.

G. Agricola [1] treated salt as a *terrarum species*. and spoke of *sal fossilis* or *Bergsaltz* ; *sal fossilis pellucens* or *sal gemma* ; *sal marinus* or *Baisaltz* or *Mersaltz* ; *sal lacustris* or *Seesaltz* ; *sal excoctus* or *Gesottensaltz* ; and *sal ammoniacus* or *sal ammoniac*. J. G. Wallerius described *Kochsalz* or *Küchensalz* (*muria, sal commune*, or *sal Agricola*) as one of four kinds of salts. Allied to rock-salt (*muria fossilis pura*, or *sal gemma*) there were *Salzerde*, *Salzstein*, *Baisaltz* (*Spanischsalz* or *Seesalz*), *muria marina* or *sal marinum*, *Strandsalz* or *Schaumsalz*, i.e. sea-salt found in some places at the bottom of the sea, or obtained by the evaporation of sea-water ; and *Brunnensalz* (e.g. *Lüneburg salt*, *muria fontana*, *sal fontanum*—obtained by the evaporation of spring water). R. J. Haüy called salt *soude muriatée* or *muriate de soude* ; E. F. Glocker proposed the term **halite** for rock-salt.

Up to the middle of the eighteenth century, the alchemists confused the sodium and potassium salts generally, and, as previously indicated, it was not until 1762 that A. S. Marggraff was able to demonstrate how the two types of salt differed, and that, usually, potassium chloride is the main product of the action of muriatic acid on the ashes of land plants. About this time, imaginary therapeutical virtues were attributed to potassium chloride, which was called *sel fébrifuge*, and *Sylvius' salt*, or *sel digestif de Sylvius*. J. G. Wallerius included Sylvius' salt among the *mineralia artificialia*, and distinguished *sal artificiale muriaticum* or artificial salt made by saturating spirit of salt with alkali, from *sal artificiale muriaticum alkali minerali præparatum* and *sal artificiale muriaticum alkali vegetabile præparatum*, or *sal regeneratum*. J. B. Romé de l'Isle said that *l'acide marin* combines with *l'alkali fixe minerale*, forming a neutral salt which is everywhere known as *sel marin* and is also called *sel gemme* ; and this acid also combines with *l'alkali fixe vegetal*, forming a neutral salt which is named *sel fébrifuge du digestif de Sylvius*, and *sel marin régénéré*. F. S. Beudant proposed the name *sylvine*, and F. S. Dana, **sylvite**, for potassium chloride.

The occurrence of sodium and potassium chlorides.—Native salt is sometimes called *halite*, but more usually *rock-salt*—in Germany *Steinsalz*, and in France *sel gemme*. It occurs in very many places, and there are immense deposits in almost every civilized country. Rock-salt is found at Winsford, Nantwich, Northwich, Middlewich (Cheshire) ; Preesal (Lancashire) ; Barrow-in-Furness (Lancashire) ; and at Stoke Prior and Droitwich (Worcestershire). Julius Cæsar [2] mentions that he found the natives of Cheshire manufacturing salt by pouring brine over charcoal faggots, and scraping off the crystals as they were formed. The Romans taught the Britons the open-pan system of evaporating brine, and this has remained the principal method of manufacturing salt down to recent days. Whence the Romans obtained the method is unknown. It is reputed to have been used in India, and in China an indefinitely long time ago. The earliest detailed description of salt-making appears in G. Agricola's *De re metallica* (Basil, 1546). Borings at Northwich show that there is a bed of salt about 75 ft. thick, about 140 ft. below the surface, beneath this there is a stratum of marls about 30 ft. thick, and then comes a second bed of rock-salt over 100 ft. thick. Below this are successive thin beds of salt and marl. The Cheshire salt-beds extend over an area of 10 by 16 miles.

The names of some localities indicate the antiquity of the salt industry, since,

in Saxon times, a place where salt was dug was called a *wich* or *wych*, and the buildings where the salt was manufactured, *wych-houses*.

The term *wich* or *wych* seems to be derived from the Anglo-Saxon *wic*, or the Norse *wig* —a dwelling-place. The hamlets established by the Norse and Dane pirates on bays and inlets were called *wigs* or *wiches*—hence the name Norwich, Sandwich—bay salt was made in these places, and hence the term *wich* came to be identified with salt, and lost its original meaning—village. In Austria and Germany, *Hall* has a somewhat analogous meaning—for instance, Halle, Hallstadt, Reichenhall, Friedrichshall, etc., are all places which have been connected with the salt industry. In England, Halsall, Halstead, and Halwick have a similar derivation. In Germany, the *Hallforst*—salt forest—supplied the salt works with wood fuel; the *Hallgraf*—salt count—possessed the mineral rights: the *Hallburg*—salt castle—was the castle where the Hallgraf lived; and workmen were called *Halloren*; and the *Heller* was a small coin used in the salt districts.

Salt is also found near Carrickfergus and Larne (Ireland); and Stassfurt (Prussian Saxony). The salt deposits near Iletz Zaschtchity (Orenberg, Russia) are said to be the richest in the world. The hill of rock-salt near Cardona (Spain) has been quarried since the time of the Romans, for Pliny mentions this deposit and said that medical men preferred salt from this locality above all others; and he added that the salt quarried from the mountain at Oromenus (India) brought a larger revenue to the exchequer than that arising from gold and pearls. The Wieliczka deposit in the Carpathians (Galicia, Austria) has been worked since the eleventh century; and it is said to be 500 miles long, 20 miles broad, and 1200 ft. thick. The galleries and chambers in this mine extend over 30 miles in length, and yield 55,000 tons of rock-salt per annum. The mine is one of the show-places for visitors in the district, for, as E. Darwin expressed it:

> Caverned round in Cracow's mighty mines,
> With crystal walls a gorgeous city shines;

and the subterranean town includes a market-place, river, and church. Salt is found in numerous other places—California, Louisiana, Utah, Kansas, New York State, Virginia, Ohio, Michigan (United States); Ontario (Canada), Mexico, etc., and in numerous localities in Asia and Africa.

Salt is very widely diffused in the waters of the globe. Most rivers carry traces, and when they discharge into land-locked basins, and when the waters are conc. by evaporation, salt-lakes are formed. The waters of the Baltic Sea contain between 0·2 and 0·8 per cent. of saline matters, whereas the waters of the Dead Sea contain up to 25 per cent. It has been estimated that next to water, salt is one of the most abundant mineral substances on the crust of the earth. The composition of the solids held in soln. in the waters of a number of oceans and seas is indicated in Table XIV.

TABLE XIV.—PERCENTAGE COMPOSITION OF THE SOLIDS IN SOLUTION IN OPEN AND CLOSED SEAS.

Waters.	Cl	Br	SO_4	CO_3	Na	K	Ca	Mg
Atlantic Ocean	55·29	0·19	7·69	0·21	30·59	1·11	1·20	3·72
Arctic Ocean	55·30	0·14	7·78	0·07	30·85	0·89	1·21	3·75
Indian Ocean	55·41	0·13	7·79	0·05	30·89	0·85	1·16	3·67
Mediterranean Sea	55·30	0·16	7·72	0·19	30·51	1·12	1·19	3·81
Black Sea	55·12	0·18	7·47	0·46	30·46	1·16	1·41	3·74
Red Sea	55·60	0·13	7·65	0·02	30·81	0·97	0·89	3·87
Dead Sea	65·81	2·37	0·31	trace	11·65	1·85	4·73	13·28
Elton Lake	64·22	—	6·82	0·04	11·27	—	0·10	17·55
Utah Lake	24·75	—	28·25	12·35	18·19	2·17	5·90	6·18
Caspian Sea	42·04	0·05	23·99	0·37	24·70	0·54	2·29	5·97
Great Salt Lake	55·99	trace	6·57	0·07	33·15	1·60	0·17	2·52
Owens Lake	25·67	—	9·95	32·51	37·38	2·18	0·02	0·01

It will be noticed that although the proportion of salts in soln. may vary from 1 to 4 per cent., the composition of the solids (*i.e.* the evaporation-residue) in open or partially closed seas is not very different. This is shown by the first six analyses in the Table XIV. When the proportion of salt is low, owing to dilution by fresh water, the proportion of lime is usually rather greater. With land-locked seas, there is no such uniformity as is observed in the ocean. Although the composition of the evaporation residue of some lakes is closely allied to that of sea-water—*e.g.* the Great Salt Lake—*each lake must be considered separately*; *the individual peculiarities are largely determined by local conditions.* At one end of the Caspian Sea, the water has a *comparatively low salinity*, 1·294; in the Karaboghaz Gulf, it is 28·50, and saline deposits are forming on the bottom. The character of the solids is also determined by the solids brought in by the feeding tributaries—*e.g.* the saline matters in the Dead Sea resemble those contained in the mother liquid of sea-water after the extraction of the sodium chloride. The water of Owens Lake yields trona on evaporation: and that of the Borax Lake (California) borax. The composition of the waters of Elton Lake varies with the season—for example, in spring the melting snow materially alters the composition of the water.

In nearly every case, the rock-salt seems to have been deposited from sea-water which must be conc. to about one-tenth its original volume before the salts begin to crystallize. The potash and magnesium salts are usually missing; as a rule, rock-salt is not accompanied by any notable quantity of these salts. The deposits at Stassfurt are rather exceptional in their completeness. Traces of potassium *salts have been precipitated with the rock-salt, although their presence is not* usually shown in the analyses. C. G. C. Bischof[3] attributed the almost complete absence of potassium chloride from rock-salt to its greater solubility in water. Gypsum is usually found either associated with the salt itself, or in the adjoining strata; if not, it is inferred that the sodium chloride is of secondary origin—possibly leached from the beds deposited elsewhere. The salt deposits of Texas and Louisiana are noteworthy in being associated with sulphur, sulphurous gases, and petroleum, but whether this deposit is of marine or volcanic origin has not been demonstrated.[4] A. W. Grabau has discussed the origin of salt-deposits.

Rock-salt occurs to a very small extent as a volcanic product, where it is probably produced by the action of hydrogen chloride present in the volcanic gas upon the lava. It is found as a white crust or loose powder in the crater. Published analyses of crater salt show that the ratio of KCl : NaCl ranges from 1 : 0·062 to 1 : 0·948. The data in Table XV are selected from published analyses of rock-salt with

TABLE XV.—THE COMPOSITION OF ROCK-SALT.

Source.	NaCl	KCl	$MgCl_2$	$CaSO_4$	$CaCl_2$	Authority.
Stassfurt . . .	97–99	—	0·03–0·25	0·20–6·35	0·04–0·53	Various sources
Wieliczka (Galicia) .	99·99	—	—	—	—	G. Bischof (1853)
Cardona (Spain) . .	98·55	—	0·01	0 44	0·99	G. Bischof (1853)
Middlesborough . .	98·42	—	0·12..	0·21	—	G. Wilson (1888)
Cheshire . . .	98·32	—	0·18	0·62	0·21	F. Dufrenoy (1845)
Goderich (Canada) .	99·69	—	0·10	0·09	0·03	T. S. Hunt (1877)
Louisiana (U.S.A.) .	98·73	—	0·01	1·19	—	F. W. Taylor (1883)
Leoncito (Argentine) .	81·49	17·48	—	1·00	—	L. Harperath (1890)
Vesuvius . . .	33·06	58·67	0·89	1·22	1·78	G. Freda (1889)

the water and insoluble matters omitted. The potassium chloride does not appear to have been determined, although, in some cases, it exceeds the amount of magnesium chloride.

Sylvine or sylvite occurs in the Stassfurt salt deposits, and it is associated with halite or rock-salt in volcanic salts; in the salt-mines of Hallem (Salzburg), Kalusz (Galicia), Mayo (Punjab), Asnapuquio (Lima, Peru), and many other places.

Published analyses of Stassfurt sylvite give a percentage composition ranging as follows:

Cl	K	Na	Mg	Ca	SO_3	H
47·2–29·3	44·8–53·2	0·3–5·5	0·01–0·2	0·07	0·003–0·5	0·38

The separation of salt from sea-water and brines.—According to Dioscorides, ἅλος ἄχνη, or the sea-foam left in-shore at high-water, on evaporation, leaves salt behind; and in Pliny's *Naturalis historia* (**31**. 39–40), it is said that salt was obtained by boiling the spring-waters of Chaonia, and that in Crete, salt was obtained by the evaporation of sea-water in salt-pans; in Cappadocia, well and spring water was similarly evaporated; and in Egypt, sea-water was allowed to overflow into enclosed basins on the sea-shores and there allowed to evaporate.

Countries not favoured with rock-salt must either import salt from more favoured countries, or resort to the conc. of sea-water, or of the brine from salt-springs, etc. Evaporation is not an expensive process in warm countries, or where coal is cheap. The brine is conc. by solar evaporation, in large hollow tanks or ponds exposed to wind and sun, on the shores of the Mediterranean and the Black Seas; on the tide-lands around San Francisco Bay; and on the banks of the brine-lakes of the United States. According to C. Ochi,[5] 10,000 tons of salt are annually extracted from the sea-water at Kaoo-Chew Bay (China).

The ponds on the Mediterranean are made from puddled clay, and called *salt meadows*, *salt gardens*, *marais salants*, or *salt ponds*. Sea-water, sp. gr. 1·026, is admitted into one pond at high tide by means of a sluice and dyke, and conc. to a sp. gr. approaching 1·210, and it at the same time deposits calcium carbonate and iron oxide. The brine is then run from the *concentration ponds* to the *crystallization ponds*, consisting of a series of rectangular compartments where the liquid is still further conc. When the sp. gr. of the brine reaches 1·285, salt of nearly 96 per cent. purity crystallizes out. A less pure salt is obtained by further concentrating the mother liquid. The crystals of salt as they separate in the crystallization pond are lifted out by means of perforated shovels, and allowed to drain alongside. The heaps of salt dry slowly, and the more deliquescent impurities—mainly magnesium chloride—are drained off, or washed out by occasional showers. An average sample contains the eq. of

NaCl	$MgCl_2$	$CaSO_4$	$MgSO_4$	Earthy matters.	Water.
95·11	0·25	1·30	0·91	0·10	2·55

The mother liquid, called *bittern*, is further conc. for crystals of *sels mixtes*—a mixture of sodium chloride with about 40 per cent. of magnesium sulphate—which, when re-dissolved in water, furnishes crystals of Glauber's salt, $Na_2SO_4.10H_2O$, on cooling to 0°: $2NaCl+MgSO_4 \rightleftharpoons MgCl_2+Na_2SO_4$. The further conc. of the brine gives a crop of crystals containing impure carnallite, $MgCl_2.KCl.6H_2O$, which is treated for potassium and magnesium salts. The mother liquid remaining after the extraction of sea-salt contains 2·3 to 3·5 per cent. of potassium chloride and magnesium sulphate and chloride. This liquid furnishes crystals of carnallite. According to F. Nishimura,[6] the separation of carnallite is very incomplete owing to the formation of a double sulphate; to avoid this, it is recommended to keep the ratio $MgSO_4 : MgCl_2$ in bittern below 0·11, by adding the mother liquor of the carnallite to the bittern. In this way, a 75 per cent. yield of carnallite can be obtained. The remaining mother liquor can be treated for bromine.

In cold countries—*e.g.* on the shores of the White Sea, or Siberia—the sea-water is conc. by freezing. The first crop of ice which separates is removed, and the residual brine is again conc. by allowing it to freeze. After removing the second crop of ice, the brine is conc. by evaporation over a fire until salt separates from the liquid.

The winning of rock-salt.—Rock-salt is often mined by bringing the solid to the surface in lumps—*e.g.* Wieliczka, Carrickfergus, etc. In some cases, the salt is mined

by forcing water down into the beds from a surface well made for the purpose—*e.g.* Cheshire, Michigan,[7] etc. The brine is afterwards pumped to the surface, and the liquid conc. in salt-ponds; or by allowing the soln. to trickle from elevated tanks over ricks of brushwood—called *graduators*—so arranged that the soln. is fully exposed to the prevailing winds; or the sat. brine may be evaporated in shallow pans—*salt-pans*—heated artificially, as is the case in Cheshire, etc. As the salt crystallizes out, it is removed by means of perforated shovels, and dried with a centrifugal machine, or on stone or iron floors heated by the waste gases from the flues below the salt-pans. If much calcium sulphate be present, it will separate first from the brine, and it must therefore be removed before the salt. The potassium and magnesium salts separate last. Natural brines are conc. in a similar manner or by solar evaporation.

Brines are also conc. by evaporation under reduced press., *i.e.* in what are called *vacuum pans* heated by steam, and specially designed to eliminate difficulties arising from the tendency of the brine to deposit a hard scale or crust of calcium salts. In some cases, the magnesium salts are first precipitated as magnesium hydroxide, $Mg(OH)_2$, by the addition of milk of lime, and the calcium sulphate subsequently removed by precipitation as carbonate by the addition of ammonium carbonate liquors. The decanted liquor is then conc. in vacuum pans.

At Carrickfergus on the Belfast Lough, the rock-salt for a time was mined and purified by a modern adaptation of an old Würtemberg process in which the mined product was conveyed to the furnaces and refined by H. Tee's process.[8] In this process, the rock-salt is crushed and melted. Air under press. is driven through the molten mass at about 930°, when the impurities are oxidized. The foreign matter settles, and the molten salt is run into a rotating pan, where it is crystallized. The salt is then conveyed to crushing and sieving machinery, where it is graded into different varieties of finished salt. The process of purification was said to occupy no more than 15 min. The process was tried in Mexico, but, in the words of W. L. Bonney, the cost rendered the experiment a failure; it could not compete with the manufacture of salt direct from brine.

If fine-grained *table salt* is needed, the brine is evaporated nearly at its b.p.; but for the manufacture of coarse-grained *fish salt*, the evaporation is conducted slowly at a comparatively low temp., 45°, so as to get the salt in comparatively large crystals. The finished salt will be contaminated with but small quantities of other salts as impurities—calcium chloride, magnesium chloride, calcium sulphate, and magnesium sulphate. Cheshire salt, for instance, contains about 98·3 per cent. of sodium chloride, and the remainder consists of insoluble matter, calcium sulphate, and magnesium and calcium chlorides. Harmless impurities may be purposely added in order to restrain the deliquescence of magnesium chloride, etc. Thus the so-called *cerebros salt* is said to contain about 3 per cent. of bone meal—calcium phosphate.

The extraction of potassium chloride from carnallite.—Potassium chloride occurs associated with magnesium chloride in carnallite, and although formerly potassium chloride was principally obtained from sea-water—*vide supra*—much of the commercial salt is now obtained from carnallite, $MgCl_2.KCl.6H_2O$, of the Stassfurt deposits. Crude carnallite contains the eq. of 16 per cent. of potassium chloride.

The crude carnallite is crushed and digested in large tanks with the mother liquid left from a preceding extraction. This liquid contains chiefly magnesium chloride. The mixture is heated by blowing in steam, and it is kept at its b.p., about 115°, until it has dissolved the maximum amount of the crude salt. Potassium chloride readily dissolves in this liquid, while most of the sodium chloride, and magnesium sulphate or kieserite, associated with the crude carnallite, remain undissolved. The liquid is allowed to settle for about an hour, and then decanted into large iron vats and the clarified liquid allowed to cool slowly. Crystals containing 64 to 69 per cent. of potassium chloride are deposited The impurities are mainly sodium chloride (20–22 per cent.), magnesium chloride (7·5 to 8·5 per cent.), and magnesium bromide and calcium sulphate (0·4 per cent.). The principles underlying the process will appear from the study of Fig. 1, Cap. XI. The crystals of potassium chloride so obtained are washed with cold water so as to remove the more soluble

sodium chloride. This process yields a product containing 85 to 98 per cent. of potassium chloride, according to the number of washings employed. The further purification of the salt involves re-solution and re-crystallization of the product. The mother liquids are worked up for more salts, and finally used for the extraction of a fresh lot of crude carnallite.

Potassium chloride is also extracted from sylvinite, a mixture of sodium and potassium chlorides, by a similar process to that used for carnallite.

The purification of the alkali chlorides.—Sodium—as well as potassium, rubidium, or cæsium—chloride can be purified by adding conc. hydrochloric acid to a cold conc. aq. soln. of the respective salts; better results are obtained by passing gaseous hydrogen chloride through the salt soln. The two chlorides are but sparingly soluble in conc. hydrogen chloride. The impurities remain in soln. while the chlorides are precipitated in a very fair state of purity. In fact, with suitable precautions—the use of platinum vessels, and of highly purified sodium carbonate as the source of the sodium chloride—an exceedingly pure salt can be obtained. A pure salt cannot be made by precipitating the impurities, but must itself be precipitated or crystallized from a less pure soln., and therefore T. W. Richards and R. C. Wells (1905) considered that this process is the best possible method of purifying sodium chloride since the included hydrochloric acid can be readily expelled by fusion. J. S. Stas[9] prepared highly purified sodium chloride in the following manner:

Purified sodium carbonate along with a little purified ammonium chloride was dissolved in water, and a stream of purified hydrogen chloride passed through the liquid. The soln. was evaporated to dryness in a platinum retort, and strongly heated to volatilize the ammonium salt. The cold mass was dissolved in water, a little purified ammonium chloride and chloroplatinate were added, on the assumption that potassium chloroplatinate would be wholly precipitated if potassium salts were present. The liquid was allowed to stand for 24 hrs. to enable any silicates or aluminates to settle. The clear decanted liquid was again evaporated to dryness in a platinum retort, and strongly heated to drive off the ammonium salts, and to decompose the platinum salt. On cooling, the still molten mass was poured into a platinum dish; and when cool, was dissolved in water. After standing a couple of days, the clear liquid was evaporated to dryness in a platinum retort, and fused. On vaporizing 10 grms. of the salt in a weighed platinum boat, J. S. Stas found that the latter gained in wt. eq. to a non-volatile impurity of 0·004 per cent.—the non-volatile residue consisted mainly of silicates of calcium and sodium.

T. W. Richards and R. C. Wells[10] have pointed out that although fused salt has but a very slight solvent action on platinum at 800°, a notable quantity is dissolved when ammonium chloride is present, and therefore Stas' test does not necessarily show the absence of a greater amount of insoluble matter than he observed, because an appreciable amount of platinum itself wonld be volatile when heated for half an hour at a high temp. However, T. W. Richards and R. C. Wells add that the impurity in Stas' sodium chloride "could hardly have exceeded 0·01 per cent." T. W. Richards and R. C. Wells omitted the ammonium chloride and chloroplatinate treatment, and prepared sodium chloride by precipitating this salt from an aq. soln. of purified sodium carbonate by means of hydrogen chloride. They then fused the dried salt; digested the cold cake in water; and, after allowing the soln. to stand for a long time, decanted the clear upper portion of the liquid. This soln. was conc. and treated with hydrogen chloride as before. No difference in the degree of purity of this salt could be detected and that of the salt prepared by repeating the treatment four times more—and the results obtained with this salt agreed with those obtained with salt prepared by the action of hydrogen chloride on purified sodium sulphate; and by the fractional crystallization of selected transparent colourless crystals of Stassfurt halite. Sodium chloride is therefore comparatively easy to purify. Fusion of the salt in vacuo gives results analogous with those obtained by fusing it in air, and it is therefore inferred that there is no risk of occluding oxygen or nitrogen; and that the water can be expelled by fusion without risk of losing the halogen.

It is very difficult to prepare sodium chloride quite free from the potassium

salt. C. Lohman[11] found commercial "chemically pure" sodium chloride to contain nearly 0·5 per cent. of potassium chloride, and this even after purification by the action of hydrogen chloride on an aq. soln. A sample prepared by dissolving metallic sodium in distilled water, and neutralizing the product with hydrochloric acid contained 0·27 per cent. The potassium was mixed with the metallic sodium. According to V. C. Shipee (1907), if the samples be recrystallized from water four times, the amount is reduced considerably below 0·03 per cent. That prepared from metallic sodium contained 0·01 per cent. of potassium chloride.

The preparation of alkali chlorides.—The chlorides are formed by the action of chlorine or hydrogen chloride on the respective metals; by the action of hydrochloric acid on the oxides, hydroxides, or carbonates; or by treating an aq. soln. of the alkali sulphate with barium chloride. The salts of the rarer metals are obtained at intermediate stages in the extraction of the metals from their ores. Most of the chlorides are conveniently purified by passing hydrogen chloride through the conc. aq. soln., and fusing the products in a quartz vessel in an atm. of hydrogen chloride, but lithium chloride is fairly soluble in aq. hydrochloric acid, although no acid salt has been prepared. The aq. soln. of lithium chloride must be evaporated with ammonium chloride, or in a stream of hydrogen chloride if hydrolysis, with the loss of hydrogen chloride, is to be prevented. H. Erdmann[12] recommends the following process for the preparation of rubidium chloride:

An intimate mixture of 274 grms. of rubidium iron alum, or 260 grms. of rubidium aluminium alum with 100 grms. of calcium carbonate, and 27 grms. of ammonium chloride, is heated in a nickel crucible to a dull red heat until ammonia vapours are no longer evolved, and then the temp. is raised to redness. The product is ground with a litre of cold water for 15 minutes; filtered by suction; and washed with 400 c.c. of water, added in small portions at a time. The combined sulphuric acid is precipitated by the addition of barium hydroxide, and the filtered liquid boiled while a stream of carbon dioxide is passed through the soln. If the soln. loses its alkaline reaction, and yet retains some calcium, a little rubidium carbonate must be added to precipitate calcium carbonate. The soln. is then treated with hydrochloric acid and evaporated.

T. W. Richards and W. B. Meldrum made highly purified lithium chloride by repeatedly evaporating the purified nitrate[13] with an excess of hydrochloric acid in a quartz dish, and then fusing the product in an atm. of hydrogen chloride. The chlorides of potassium, rubidium, and cæsium have also been purified by precipitating with hydrochloroplatinic acid, calcining the alkali chloroplatinate, and extracting the chloride with water.

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§ 15. The Properties of the Alkali Chlorides

The **crystals** of rock-salt are nearly always cubes or small octahedrons. When the crystals form on the surface of evaporating brine, distinctive hopper-shaped crystals resembling hollow quadrilateral pyramids are developed; the inner surface appears to be arranged in a series of steps. D. I. Mendeléeff [1] explains the formation of hopper salt crystals as follows:

If a soln. of sodium chloride be slowly heated from above, where the evaporation takes place, the upper layer will become sat. before the lower and cooler layers, and therefore crystallization will begin on the surface, and the crystals first formed will float—having also dried from above—on the surface until they become quite soaked. Being heavier than the soln. the crystals are partially immersed in it, and the following crystallization, also proceeding on the surface, will only form crystals by the side of the original crystals. A funnel is formed in this manner. It will be borne on the surface like a boat (if the liquid be quiescent) because it will grow more from the upper edges. We can thus understand this, at first sight, strange funnel-form of crystallized salt. To explain why the crystallization under the above conditions begins at the surface and not at the lower edges, it must be mentioned that the sp. gr. of a crystal of sodium chloride is 2·16, and that a soln. sat. at 25° contains 26·7 per cent. of salt and has a sp. gr. 1·2004 at 25°; at 15° a sat. soln. contains 26·5 per cent. of salt, and has a sp. gr. 1·203 at 15°. Hence a soln. sat. at a higher temp. is specifically lighter, notwithstanding the greater amount of salt it contains. With many substances surface crystallization cannot take place because their solubility increases more rapidly with the temp. than their sp. gr. decreases. In this case the sat. soln. will always be in the lower layers, where also the crystallization will take place.

According to W. L. Bragg,[2] the **X-ray spectrograms** indicate that the arrangement of the atoms of the alkali halides is that of a simple cubic lattice, and where the atoms are nearly all equal in size, the symmetry is cubic holohedral—*e.g.* sodium chloride—and plagihedral when the atoms are markedly different in size—*e.g.* potassium chloride, or bromide. W. P. Davey and F. G. Wick obtained similar results with cæsium chloride. K. Fajans and K. F. Herzfeld give for the distances apart of the atoms in the **space lattice** of sodium, potassium, and rubidium chlorides *respectively* $2·817\times10^{-8}$, $3·141\times10^{-8}$, *and* $3·286\times10^{-8}$ *cm., and for the respective* lattice energies, 170·0, 159·0, and 154·6 Cals. per mol.

The crystals have a cubic cleavage, and if a punch with a rounded end is placed against a cleavage face, and struck lightly with a hammer, two cracks are produced perpendicular to the surface, and each crack is parallel to a diagonal of the cubic face so as to form a four-rayed star. When mica is similarly treated, a six-rayed star is produced. These cracks form what are called **impact or percussion figures**—*Schlagfiguren.* If a cube of salt is placed diagonally in a vice, and compressed, the cube falls into two pieces along a diagonal parallel to a face of the rhombic dodecahedron. One half of the crystal slides over the other half, and the plane of gliding is called a **gliding plane**—*Gleitflache.* Again, if a cube of salt is exposed to moist air, a film of moisture is deposited on the surface, and small pits or square pyramids are etched into a cleavage or natural face of the crystal—**etched figures.**

G. Tammann found that potassium and sodium chlorides form a continuous series of mixed crystals between 660° and 500°. Since neither salt has a transition point, the phenomena observed when the mixed crystals are cooled must be attributed to separation of the components. With diminishing temperature, therefore, either the attractive forces within the molecules of the respective chloride must increase, or those between the unlike molecules must be greatly weakened. The results obtained by etching the individual crystals at the ordinary temperature indicate that the intra-molecular forces of the potassium chloride crystals differ from those of the sodium chloride crystal, or, more precisely, that certain lattice regions are more closely united in the former, whilst such differences are not observed in the latter. *In the light of these observations, it is surprising that the X-ray analysis* indicates the same lattice for each crystal.

The native crystals of rock-salt are either colourless or vary in tint from white, to dirty grey, to yellow, to reddish-yellow, and sometimes blue or purple. The colours are usually produced by impurities mixed with the salt at the time of deposition—ferric oxide gives a reddish colour; clay or anhydrite a grey colour; and organic matter a brown colour. In some cases these impurities have been deposited in layers parallel to the faces of the cube giving a series of light and dark striations. The deep-blue colour sometimes found in the salt of various mines has attracted attention from the beginning of the nineteenth century; it is mentioned in H. Davy's letters (1818). The cause of the coloration of **blue salt** cannot be traced by analysis to the presence of any known impurity; and, as usually occurs in the absence of positive evidence, numerous tentative explanations have been suggested.[3] The colour has been attributed to the presence of organic matter (L. Wohler and H. Kasarnowsky); to the presence of an alkali subhalide (E. Wiedemann and G. C. Schmidt); to the presence of an allotropic modification of the chloride (E. Goldstein); to a solid soln. of the metal in the salt (J. Elster and H. Geitel); and to the presence of ultra-microscopic or colloidal particles of the free metal (R. Zsigmondy)—smaller than $0·4\mu$. The blue colour seems to disappear in time, and also when the salt is recrystallized from water, or heated above 280°. The natural colour can be nearly reproduced by the action of the vapour of the metal on the halide at a high temp.; and by exposing a colourless crystal to the Röntgen or Becquerel rays, to radium emanation, or to cathode rays. According to E. Newbery and H. Lupton, rock-salt is coloured brown throughout its mass by exposure to the action of radium emanation, while exposure to cathode rays gives a brown coloration on the surface; sylvine is coloured blue by radium; the colour is evanescent, and disappears in a few hours—even in darkness. Cathode rays colour sylvine or purified potassium chloride violet. The blue colour acquired by salt in the cathode rays loses its electric charge more rapidly in light than in darkness. Colourless sodium chloride, however, crystallizes from a soln. of sodium chloride in ammonia, but the organosol of sodium is blue. The blue colour is not affected by boiling the salt with alcohol; or heating it with mercury. According to E. Pieszczek (1906), analyses of blue-coloured rock-salt show 0·4 per cent. less chloride than the colourless salt, the failure of chlorine to restore the colour is said to be due to the protective action of films of the halide itself. According to R. Abegg (1897), an aq. soln. of the coloured salt is not alkaline, and does not exert a reducing action.

When molten sodium chloride is exposed to the action of potassium vapour, some potassium chloride and sodium are formed, and H. Rose[4] obtained a dark-blue mass supposed to be **potassium subchloride,** K_2Cl, by melting potassium with potassium chloride in a stream of hydrogen; sodium chloride and sodium under similar conditions furnish a yellowish-brown mass supposed to be **sodium subchloride,** Na_2Cl. The coloured mass is decomposed into the alkali chloride and hydroxide and hydrogen when treated with water. Two years earlier, G. Kirchhoff and R. Bunsen also obtained colourless masses about the cathode during the electrolysis of molten rubidium and cæsium chlorides; H. Moissan also prepared what he considered to be bluish-green **rubidium subchloride,** Rb_2Cl, by treating rubidium hydride with hydrogen chloride gas; and with cæsium hydride under similar conditions, orange-yellow **cæsium subchloride,** Cs_2Cl, was formed. According to L. Wohler and H. Kasarnowsky, the yellowish-brown colour of the supposed sodium subchloride, the violet colour of potassium subchloride, and the sapphire blue of rubidium subchloride are removed by heating the respective substances to 570°, 460°, and 420°, whereas the blue colour of native rock-salt is lost at 275° (as samples coloured artificially are decolorized at 400°). A. N. Guntz also thought that he had prepared **lithium subchloride,** Li_2Cl, by heating a mixture of lithium chloride or lithium and potassium chloride with lithium carbide; and by treating lithium chloride with lithium as in H. Rose's process. Later, however, he found that the product is not lithium subchloride, Li_2Cl, but rather a mixture of lithium hydride and chloride. Attempts were made to prepare this salt by heating a mixture of lithium hydride and chloride at 880° under reduced press. by heating a mixture of lithium chloride and lithium in the presence of argon; and by heating a mixture of lithium and lithium chloride in a hermetically sealed steel bomb, but the results neither proved nor disproved the presence of small quantities of the subchloride.

H. Rose's assumption that the coloured mass obtained by heating the alkali chloride with the vapour of the metal contains the alkali subchloride, was largely based on the fact that no sign of a metallic substance can be detected by the naked eye, or under the microscope. This evidence has very little value to-day. L. Wöhler and H. Kasarnowsky have emphasized the fact that, unlike aq. soln. of native salt, the artificially coloured halides give alkaline soln., and since analyses of the natural salt gave the eq. of about 0·016 per cent. of carbon and 0·008 per cent. of hydrogen, it is supposed that the coloration arises from different causes in the two cases. The blue coloration of native salt is said to be due to the presence of traces of organic matter, and the artificially coloured salt to a trace of metal or subchloride in colloidal solid soln. R. Lorenz's *Metallnebel*[5]—metal fogs—which are formed during the electrolysis of fused metallic salts, appear to be analogous colloidal soln.—probably of the metal in the salt. R. Zsigmondy believes that the evidence favours the hypothesis that the alleged subchlorides, as well as the blue-coloured chlorides, are in all probability colloidal soln. of the metal in the chloride, all the more so as J. Bronn has shown that the coloured soln. of the alkali metals in liquid ammonia are colloidal.

The blue luminescence observed by E. Wiedmann and G. C. Schmidt[6] during the action of cathode rays on the alkali halides is probably due to the slight decomposition into sodium and chlorine by the cathode rays and their subsequent recombinations to produce the blue luminescence; if some chlorine escapes, the free sodium remains in colloidal soln. producing the blue salt. This is confirmed by E. F. Farnau's observation that salts which have been exposed to the cathode rays can be made temporarily luminescent by heat; the heat presumably accelerates the speed of recombination, and so augments the intensity of the light emitted; the colour of the emitted rays is the same as that produced during the action of the cathode rays on the salts. A. Arnold and G. C. Schmidt found that when sodium salts are exposed to the anode or canal rays, they emit first a blue luminescence like the cathode rays; this is soon replaced by a reddish-yellow light in which the yellow *D*-lines of sodium appear. These rays are more violent in their action than the cathode rays; after the exposure, the heating of the salt produces a blue thermoluminescence. J. J. Thomson found that when lithium chloride is alternatively exposed to the action of anode and cathode rays in the same tube, the anode rays produce a bright red luminescence showing the characteristic lithium line, while the cathode ray luminescence is steely blue, with a faint continuous spectrum.

The **crystalloluminescence** of the alkali halides was first noted by E. Bandrowsky,[7] who observed the phenomenon during the rapid precipitation of sodium chloride by alcohol or hydrochloric acid. M. Trautz showed that, in general, the intensity of the luminescence increases with increasing reaction velocity. E. F. Farnau recommends conc. acid; E. Bandrowsky, 23 per cent. acid; and H. B. Weiser showed that no light is obtained by precipitating the salt from a sat. soln. with acid of sp. gr. 1·1045, the light is brightest with acid of sp. gr. 1·1190; and faint with acid of sp. gr. 1·1890; similarly with alcohol of sp. gr. 0·804, a brighter glow was obtained than with alcohol of less or greater sp. gr. M. Trautz and H. B. Weiser also emphasized rapidity of mixing by agitation in order to get the best results; the presence of gelatine decreases or prevents the luminescence. The slowness of the reaction at a low temp. may produce a less intense luminescence than at a higher temp., otherwise, the brightest glow occurs at 0°—better results were obtained at 25° than at 0° or 50°. E. Bandrowsky supposed that the light was white like an electric spark, but H. B. Weiser showed that the colour is bluish-white, and that the colour of the luminescence when sodium burns in air is similar, but slightly bluer than the crystalloluminescence of sodium chloride. E. Bandrowsky obtained similar results with potassium chloride and bromide, and E. F. Farnau with the halides of the five alkali metals.

The alkali chlorides—and indeed the alkali halides—form two groups: I. The

lithium and sodium salts; and II. The potassium, rubidium, and cæsium salts. In spite of the close crystallographic relationships between the halides of potassium and those of sodium or lithium, P. Groth[8] considers that these salts are not isomorphous. This view is mainly founded on the work of R. Krickmeyer in which no signs of the formation of mixed crystals or solid soln. were observed when the halides sodium and potassium were simultaneously crystallized from an aq. soln. However, N. S. Kurnakoff and S. F. Schemtschuschny[9] have shown that sodium and potassium chlorides do form mixed crystals which are stable only at temp. exceeding 400°. E. Jänecke found a minimum in the fusion curve of mixtures of the two salts under press.; he has followed the whole course of the "unmixing" curve of the mixed crystals of cooling mixtures of the two salts. There is no reason for doubting the isomorphism of the halide salts of potassium, rubidium, and cæsium. These salts are miscible with one another and form solid soln. as indicated in Table IV. The failure of the sodium-lithium group to form isomorphous mixtures with the potassium groups is not surprising in view of the marked differences in the mol. vol. of the two groups as exemplified in the subjoined scheme where the difference between two adjoining numbers—vertical or horizontal—are represented in smaller type.

TABLE XVI.—MOLECULAR VOLUMES OF THE ALKALI HALIDES.

	Li		Na		K		Rb		Cs	NH_4
Chlorides . .	20·5	6·5	27·0	10·4	27·4	5·6	43·0	−0·8	42·2	34·0
	4·4		5·0		6·5		5·9		5·2	
Bromides . .	24·9	7·1	32·0	10·9	42·9	6·0	48·9	−1·5	47·4	39·6
	7·8		8·7		9·7		10·2		0·4	
Iodides . .	32·7	8·0	40·7	11·9	52·6	6·5	59·1	−2·3	46·8	57·5

The differences between the mol. vol. of the sodium and the potassium salts are markedly greater than between the members of each group. It will also be observed that replacing chlorine by bromine increases the mol. vol. of the halide salts by approximately the same unit; this is also the case when bromine is replaced by iodine, but the substitution of bromine by iodine produces a larger increase than the substitution of chlorine by iodine. The mol. vol. of cæsium halides is much smaller than would have been anticipated by analogy with the other members of the series. It is doubtful if ammonium belongs to the potassium group in spite of the crystal symmetry.

A great deal of work has been done on the influence of different substances in soln. on the crystal form of the sodium or potassium chloride.[10] Hydrochloric and nitric acids; potash or soda lye; aqua ammonia; boric or oxalic acid; and the chlorides of zinc, nickel, cobalt, and manganese have no effect in that cubic crystals are formed. Urea, calcium, or magnesium chloride or nitrate, phosphoric acid, and chromic or cadmium chloride, give some octahedral crystals of sodium chloride; potassium iodate or carbonate or lead chloride give some octahedral crystals of potassium chloride; barium antimonyl tartrate gives rhombic dodecahedra with sodium chloride; and lead oxide or mercury chloride gives similar crystals with potassium chloride; carbohydrates and urine give icositetrahedral crystals with potassium chloride.

Natural crystals often have enclosures containing gases or colourless liquid. The walls of the cavities are parallel to the faces of the cube. The liquid is usually an aq. soln. of brine, and the gases often confined under considerable press. usually hydrocarbons. When such crystals are dissolved in water, the gas escapes with a crackling noise when the cavity walls have become so thin that they cannot withstand the internal press. When the salt is heated, too, the expansion of the gas or liquid in the cavities bursts the mass, scattering the fragments in all directions.

The salt is then called **decrepitating salt**—*Knistersalz*. Salt which has been rapidly crystallized is much more liable to decrepitate than salt which has been slowly crystallized—presumably because it is more liable to include traces of the mother liquid.

The **specific gravities** of the five alkali chlorides by G. P. Baxter and C. C. Wallace [11] are :

Temp.	LiCl	NaCl	KCl	RbCl	CsCl
70·19°	2·059	2·153	1·978	—	3·952
50·04°	2·063	2·156	1·981	2·792	3·961
25·00°	2·068	2·161	1·987	2·798	3·974
0°	2·073	2·168	1·992	2·806	3·988

The sp. gr. of sodium chloride after melting and rapid cooling is 2·125 ; and with slow cooling, 2·150. In 1690, R. Boyle gave 2·143 for the sp. gr. of *sel gemme*.

F. L. Haigh gives for lithium chloride, 2·068 (20°/4°) ; H. G. F. Schröder gives for sodium chloride, 2·074 (3·9°) ; P. Kremers, 1·998 (17·5°) ; and G. P. Baxter, 2·068 (25°). J. W. Retger's value for sodium chloride is 2·167 (17°) ; and R. Krickmeyer's, 2·174 (20)° ; F. W. Clarke's, 2·06 to 2·16. J. Y. Buchanan's value for potassium chloride is 1·951 (23·47°) ; J. W. Retgers', 1·989 (16°) ; R. Krickmeyer's, 1·994 (20°) ; F. W. Clarke's, 1·836–1·995 ; and J. Johnston and L. H. Adams', 1·984 (30°). For rubidium chloride, H. G. F. Schröder found 2·209 (22°) ; F. L. Haigh, 2·762 (20°/4°) ; J. Y. Buchanan, 2·706 (29·9°) ; E. H. Archibald, 2·753 ; and C. Stetterberg, 2·807. For cæsium chloride, C. Setterberg found 3·992 ; F. L. Haigh, 3·987 (20°/4°) ; J. Y. Buchanan, 3·982 (23·1°) ; and T. W. Richards and E. H. Archibald, 3·972 (20°).

F. L. Haigh also worked out Valson's moduli for these salts. According to G. Quincke, the sp. gr. of the salts at their m.p. are LiCl, 1·515 ; NaCl, 1·612 ; and KCl, 1·612 : some of J. M. Jäger's values are indicated in Table XVII. He gives for the sp. gr. of molten lithium chloride at $\theta°$ (water at 4° unity), $D=1·798-0·000432(\theta-600)$; sodium chloride, $D=1·549-0·0006261(\theta-800)$; potassium chloride, $D=1·539-0·0005947(\theta-750)$; rubidium chloride, $D=2·129-0·000823(\theta-700)$; and cæsium chloride, $D=2·786-0·00108(\theta-650)$. E. M. Brunner found sp. gr. of molten sodium chloride between the m.p. and 1000° to be $1·500-0·00054(\theta-900)$; potassium chloride, $1·450-0·00057(\theta-900)$; and of lithium chloride, $1·375-0·00943(\theta-900)$. W. Biltz, and K. Fajans and H. Grimm studied the mol. vol. of the alkali chlorides.

W. Spring [12] found the difference between the sp. gr. of potassium chloride before and after compression at 20,000 atm. is small and irregular, and is probably due to experimental error ; and J. Johnston and J. H. Adams showed that if the crystals are free from cracks and holes, there is no evidence of any change in the sp. gr. of potassium chloride, bromide, iodide, or sulphate, and of ammonium sulphate with press. J. H. Hassenfratz inferred that the sp. gr. of powdered glass is different when in large and in small pieces, and G. Rose made some observations on this subject, but in neither case is any definite conclusion to be drawn. Earl of Berkeley found no measurable difference in the case of barium sulphate, but W. Spring said that the sp. gr. increases as the grain-size decreases. H. E. Merwin obtained no difference in the case of clear quartz, and J. Johnston and L. H. Adams observed no difference in the case of potassium chloride, or sulphate, and with quartz, provided the material is free from cracks and holes ; but if the material is not homogeneous, the fine powder is denser than the coarse.

G. Quincke's value for the **capillary constant** [13] of molten lithium chloride is $a^2=8·53$ sq. mm. ; sodium chloride, $a^2=8·41$ sq. mm. ; and potassium chloride $a^2=8·76$ sq. mm. The **surface tension** of molten lithium chloride is 63·4 dynes per cm., sodium chloride 66·5 ; and potassium chloride, 69·3 dynes per cm. According to J. M. Jäger, the surface tension (ergs per cm.), sp. gr. (θ/4°), and mol surface energy (ergs per sq. cm.) of the molten salt, are indicated in Table XVII.

TABLE XVII.—SURFACE TENSION AND SPECIFIC GRAVITIES OF THE MOLTEN ALKALI CHLORIDES.

	Temp.	Surface tension.	Sp. gr.	Mol. surface energy.	Temp. coeff. per deg.
LiCl	614°	137·8	1·496	1282·0	0·47
	1074·6°	104·8	1·296	1072·9	0·47
NaCl	802·6°	113·8	1·547	1281·5	0·48
	1171·8	88·0	1·316	1103·8	0·48
KCl	799·5°	95·8	1·509	1290·0	0·68
	1167°	69·6	1·287	1042·1	0·68
RbCl	750°	95·7	2·088	1433·4	1·02
	1150°	61·4	1·759	1034·5	1·02
CsCl	663·7°	89·2	2·772	1378·0	0·72
	1080°	56·3	2·332	975·8	0·36

T. W. Richards and G. Jones' value for the **compressibility** of solid sodium chloride at 20° between 100 and 500 atm. is $4·1\times10^{-6}$ megabars, and of potassium chloride, $5·0\times10^{-6}$ megabars. L. H. Adams and co-workers found for the compressibility of sodium chloride $4·12\times10^{-6}$ at atm. press., and $3·53\times10^{-6}$ at a press. of 10,000 megabars per sq. cm.; and for the change in vol.,

$$dv=-0·89\times10^{-4}+4·006\times10^{-6}(p-p_0)+2·95\times10^{-11}(p-p_0)^2.$$

The compressibility of aq. soln. of lithium and sodium chlorides has been studied by W. C. Röntgen and J. Schneider; O. Schmidt also studied soln. of lithium chloride; and M. Schumann, H. Gibault, and F. Pohl, soln. of sodium, potassium, rubidium, and cæsium chlorides; in addition, J. Drecker studied soln. of potassium chloride, and C. Grassi of sodium chloride—*vide* Table XVII. and ammonium iodide. N. Voigt gave 0·00042; and W. C. Röntgen and J. Schneider, 0·00050, for the compressibility coeff. of sodium chloride; and respectively 0·000745 and 0·00056 for potassium chloride. The elastic constants are greatest when taken perpendicular to the cubic faces, and least, perpendicular to the rhombic dodecahedral face. The **elastic modulus** of crystals of sodium chloride measured by W. Voigt for the cubic c, the octahedral o, and the dodecahedral g surfaces, in kgrms. per sq. mm., are $E_c=4187$; $E_d=3490$; and $E_o=3026$; and likewise for potassium chloride, $E_c=3724$; and $E_d=1960$; K. R. Koch gave $E_c=4033$; and $E_g=3395$ for sodium chloride, and $E_c=4010$; and $E_d=2088$ for potassium chloride. W. Voigt gave T_c 1294 for the **torsion modulus** of sodium chloride, and 655 for potassium chloride, $\epsilon=E^{-1}=\{33·48-9·66(\alpha^4+\beta^4+\gamma^4)\}\times10^{-5}$, the modulus of extension of sodium chloride, and $\epsilon=E^{-1}=\{75·1-48·2(\alpha^4+\beta^4+\gamma^4+)\}\times10^{-5}$ for potassium chloride; $\tau=T^{-1}=\{154·58-77·28(\beta^2\gamma^2+\gamma^2\alpha^2+\alpha^2\beta^2)\}\times10^{-5}$ for the torsion coeff. of sodium chloride, and $\tau=T^{-1}=\{306·0-385·6(\beta^2\gamma^2+\gamma^2\alpha^2+\alpha^2\beta^2)\}\times10^{-5}$ for potassium chloride. W. Voigt also gave $c_{11}=4770$, $c_{44}=1294$, and $c_{12}=1320$ for the elastic constants of sodium chloride, and $c_{11}=3750$, $c_{44}=655$, and $c_{12}=198$ for potassium chloride. K. Försterling has compared the elastic constants of potassium chloride with results deduced from the space lattice theory. K. Dörsing, T. Martini, and G. Wertheim measured the **velocity of sound** in soln. of sodium chloride of different conc., and found that it increased with conc.

The **hardness** of sodium chloride is nearly 2, and it is a little harder than gypsum. The hardness of a cubic face of the crystal is less than that of an octahedral face and the hardness of a dodecahedral is intermediate between the two.

The best representative values of the **melting and boiling points** of the alkali chlorides [14] are:

	LiCl	NaCl	KCl	RbCl	CsCl
M.p.	614°	801°	790°	714°	647°
B.p.	1360°	1490°	1500°	—	—

The number for the m.p. of lithium chloride reported by T. Carnelley is 600°; K. Hüttner and G. Tammann, 605°–607°; E. Korreng, 609°; K. Hachmeister, 605°; T. W. Richards and W. B. Meldrum, 613°; G. Scarpa, 605°; and by S. F. Schemtschuschny and F. Rambach, 614°. W. Ramsay and N. Eumorfopoulos' value 491° is too low. T. Carnelley gave 772°–776° for sodium chloride; V. Meyer and W. Riddle, 815·4°; H. le Chatelier, 780°; J. McCrae, 811° to 814·5°; W. Ramsay and N. Eumorfopoulos, 733°; O. Ruff and W. Plato, 820°; K. Hüttner and G. Tammann, 810°; K. Arndt, 805°; and W. P. White, 801°. W. Truthe, C. Sandonnini, and G. Scarpa, 806°; O. Menge, 803°; for potassium chloride, W. Ramsay and N. Eumorfopoulos give 762°; W. Plato, 772·3°; K. Hüttner and G. Tammann, 778°; K. Arndt, 775°; T. Carnelley, 734°; V. Meyer and W. Riddle, 800°; O. Menge and C. Sandonnini, 776°; W. Truthe, 775°; S. F. Schemtschuschny and N. S. Kurnakoff, 790°; T. W. Richards and W. B. Meldrum, 773°; and H. le Chatelier, 740°. The m.p. of rubidium chloride according to T. Carnelley is 710°; S. F. Schemtschuschny and F. Rambach, 726°; T. W. Richards and W. B. Meldrum, 714°; and K. Hüttner and G. Tammann, 712°–713°; for cæsium chloride, T. Carnelley and W. C. Williams give 631°±3°; E. Korreng, 635°–638°; C. Sandonnini and G. Scarpa, 639°; T. W. Richards and R. Meldrum, 645°; and S. F. Schemtschuschny and F. Rambach, 646°.

The b.p. indicated above are by L. H. Borgström; W. R. Mott gave 1300° and 1200° respectively for the b.p. of potassium and sodium chlorides. Lithium, sodium, and potassium chlorides begin to sublime at their m.p.,[15] and probably also the other salts as well.

Lithium chloride has been volatilized completely in a stream of hydrogen chloride at a white heat. These salts also volatilize in the hottest part of a Bunsen flame, and under these conditions R. Bunsen found potassium chloride volatilized 0·776 times as fast as the same amount of sodium chloride. T. H. Norton and D. M. Roth say 0·923 times as fast. The relative density of the vapour of sodium chloride has been determined. Potassium chloride loses weight six times more quickly when heated to bright redness in a stream of moist air than it does in dry air.[16] There is a slight loss by volatilization of salt *entraîné avec la vapeur d'eau*, during the evaporation of aq. soln. of the alkali chlorides; G. H. Bailey[17] found that during the evaporation of a litre of water from soln. to which water was added from time to time to keep the volume approximately 100 c.c. and the conc. that stated in brackets:

	$LiCl(\frac{1}{10}N)$	$NaCl(\frac{1}{10}N)$	$KCl(\frac{1}{10}N)$	$RbCl(\frac{1}{4}N)$	$CsCl(\frac{1}{4}N)$
Loss, mgrms. . .	0·25	0·81	1·22	2·95	3·21

The typical **V**-curve for eutectic mixtures is obtained with mixtures of potassium chloride with 39 per cent. of potassium fluoride at 605°; 76 of potassium bromide at 740°; 69·3 of potassium iodide at 580°; and 42·8 of potassium sulphate at 705°. Results with binary mixtures of the alkali chlorides are indicated in the accompanying Table XVIII, where the eutectic temp. is bracketed with the atomic percentage of the element indicated on the same horizontal line; *S* means that an unbroken series of solid soln. are formed; otherwise, solid soln. are wanting.

TABLE XVIII.—BINARY MIXTURES OF THE ALKALI CHLORIDES.

Chloride.	Li	Na	K	Rb	Cs
Li	—	*S* 27·0 (552°)	— 40·5 (358°)	— 41·7 (318°)	— 59·3 (323°)
Na	*S* 73·0 (552°)	—	*S* 50·0 (664°)	— 55·0 (541°)	65·5 (451°)
K	— 59·5 (352°)	*S* 50·0 (664°)	—	*S* No eutectic	*S* 66·0 (616°)
Rb	— 58·3 (312°)	45·0 (541°)	*S* No eutectic	—	*S* 88·5 (635°)
Cs	— 40·7 (323°)	— 34·50 (451°)	*S* 34·0 (616°)	*S* 11·5 (636°)	—

The chlorides of potassium, rubidium, and cæsium form binary mixtures miscible in all proportions, but the binary mixtures LiCl—NaCl, and NaCl—KCl form a limited series of mixed crystals. According to R. Nacken,[18] in the latter case, pure sodium chloride can exist below 300° and potassium chloride below 250°. Potassium and lithium chlorides give a sharp eutectic at 361° with 58·5 mols. per cent. of the *lithium salt. With rubidium or cæsium chloride with lithium chloride the cusp at* the eutectic is cut off owing to the formation of a new solid phase, for, in the case of rubidium and lithium chlorides, there is a peritectic point at 323°, with 53·8 per cent. of lithium chloride corresponding with the formation of the compound RbCl.LiCl, or **rubidium chlorolithiate,** $RbLiCl_2$; and with lithium and cæsium chlorides, there is a peritectic point at 351°, with 46·5 per cent. of lithium chloride corresponding with the compound LiCl.CsCl, or cæsium dichlorolithiate, $CsLi.Cl_2$; and another corresponding with the formation of cæsium trichlorolithiate, LiCl.2CsCl. According to T. W. Richards and W. B. Meldrum, potassium chloride raises the m.p. of rubidium chloride. The heating or cooling curve of cæsium chloride shows that cæsium chloride melts between 635° and 638°, and suffers an enantiotropic change: α-CsCl$\rightleftharpoons\beta$-CsCl, at 459° as illustrated by E. Korreng's curve, Fig. 19. C. Sandonnini and G. Scarpa place the transformation temp. at 450°; and S. F. Schemtschuschny and F. Rimbach, at 451°. Both forms belong to the cubic system. The equilibrium diagram for the binary system: LiCl—CsCl, worked

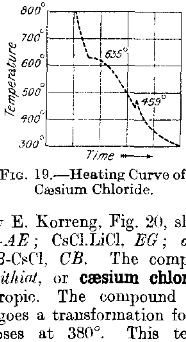

FIG. 19.—Heating Curve of Cæsium Chloride.

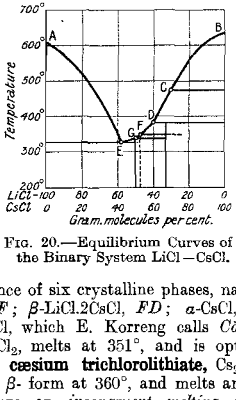

FIG. 20.—Equilibrium Curves of the Binary System LiCl—CsCl.

out by E. Korreng, Fig. 20, shows the existence of six crystalline phases, namely, LiCl—*AE*; CsCl.LiCl, *EG*; α-LiCl.2CsCl, *GF*; β-LiCl.2CsCl, *FD*; α-CsCl, *DC*; and β-CsCl, *CB*. The compound, LiCl.CsCl, which E. Korreng calls *Cäsiumchlorolithiat*, or **cæsium chlorolithiate,** $CsLiCl_2$, melts at 351°, and is optically anisotropic. The compound LiCl.2CsCl or **cæsium trichlorolithiate,** Cs_2LiCl_3, undergoes a transformation form, an α- to a β- form at 360°, and melts and decomposes at 380°. This temp. is therefore an *incongruent melting point*: β-LiCl.2CsCl=0·561α-CsCl+1·439CsCl+LiCl. Both forms of the trichlorolithiate are doubly refracting, but the α-form is less so than the β-form; both forms are deliquescent. The crystals of the two trichlorolithiates, unlike the dichlorolithiate, exhibit repeated twinning.

D. D. Jackson and J. J. Morgan represented the **vapour pressure** of potassium chloride between 801° and 1500° by $\log p=-5326T^{-1}+1{\cdot}75\log T+0{\cdot}000511T-0{\cdot}7064$ when p is expressed in mm. of mercury. The observed values were 1·54 mm. at 801°; 8·33 mm. at 948°; and 24·1 mm. at 1044°. L. H. Borgström found the **boiling point** to be 1500° at 760 mm.; 1490° for sodium chloride; and 1360° for lithium chloride.

No peritectic point was noticed with lithium chloride and potassium or sodium chlorides. T. W. Richards and W. B. Meldrum (1917) have also studied ternary mixtures of lithium and sodium chlorides with potassium, rubidium, or cæsium

chloride. No mixed crystals were obtained by R. Krickmeyer with mixtures of potassium and sodium chlorides, lithium chloride, or ammonium chloride. W. Ostwald and N. N. Beketoff have shown that the heat of soln. of a mixture of the two salts which has been previously fused is greater than a mechanical mixture which has not been fused—with a mol. each of sodium and potassium chloride in 100 mols. of water, the heat of soln. in the former case is —5·02 Cals. or even —3·62 Cals., and in the latter case —5·70 Cals. When the fused mixture is powdered and kept at about 200°, it gradually approximates to the value for a mechanical mixture. N. S. Kurnakoff and S. F. Schemtschuschny found that a recently melted mixture of the two salts gives no eutectic if it has been rapidly cooled, and that the cooling curve gives a singularity between 320° and 406°. This is believed to indicate that the two chlorides are quite miscible and form a solid soln. at high temp., and that the solid splits into its two constituents at about 400°. G. Scarpa found that with binary mixtures of lithium hydroxide and chloride there is a eutectic at 290° with 50 mols. per cent. of lithium hydroxide. There is an arrest at about 285° corresponding with **lithium dihydroxytrichloride,** 2LiOH.3LiCl, which decomposes on melting. The transformation point of sodium or potassium hydroxide is lowered by the corresponding chloride; binary mixtures of sodium hydroxide and chloride and of potassium hydroxide and chloride gave two series of mixed crystals with a miscibility break corresponding with H. W. B. Roozeboom's type IV.

G. Bartha gave the **boiling point** of the metal chloride in the cathode light as 1005° for lithium chloride; 850° for sodium chloride; 800° for potassium chloride; 790° for rubidium chloride; and 750° for cæsium chloride.

The **heat of fusion** of potassium chloride is 86·0 cals. per gram, and of sodium chloride 123·5 cals. per gram.,[19] and the **latent heat of vaporization** of sodium chloride is 3·53 Cals. D. D. Jackson and J. J. Morgan gave 30·800 Cals. for the latent heat of vaporization of potassium chloride; while A. von Weinberg gave 48·2 Cals. for the heat of sublimation of potassium chloride, and 48·8 Cals. for that of sodium chloride; and A. Reis calculated 58 Cals. for sodium chloride; 52 Cals. for potassium chloride; 50 Cals. for rubidium and cæsium chloride; and between 15 and 35 Cals. for lithium chloride. The **specific heat** of the anhydrous lithium chloride between 13° and 97° is 0·2821; according to H. Kopp, the value for sodium chloride between 13° and 45° is 0·216; and, according to H. V. Regnault, 0·213 between 13° and 46°; and 0·21401 between 15° and 98°. For potassium chloride between 13° and 46°. H. Kopp gives 0·171; H. V. Regnault, between 14° and 99°, 0·1730; and W. Plato, between 20° and 726°, 0·1840, and for the molten chloride between 807° and 935°, 0·2671. For rubidium chloride between 16° and 45°, H. Kopp gives 0·112. J. N. Brönsted gives values for the sodium to cæsium chlorides between 0° and 20°:

	LiCl	NaCl	KCl	RbCl	CsCl
Sp. ht.	(0·2821)	0·2027	0·1614	0·1013	0·0746
Mol. ht.	(80·4)	11·85	12·04	12·25	12·56

F. Koref found the sp. ht. and mol. ht. of sodium chloride between —188·1° and —81·0° to be respectively 0·1664 and 9·73; and between 0° and —75·2°, 0·1971 and 11·52; similarly for potassium chloride, between —191·7° and —81·1°, 0·1410 and 10·50; and between 0° and —76·6°, 0·1581 and 11·78. According to W. Nernst, the mean mol. ht. of sodium chloride is:

	25·0° K.	28·0° K.	67·5° K.	81·4° K.	83·8° K.
Mean mol. ht.	0·29	0·40	3·06	3·54	3·82

while the mol. ht. of potassium chloride is:

	22·8° K.	30·1° K.	48·3° K.	57·6° K.	70·0 K.	86° K.	290° K.
Mean mol. ht.	0·58	0·98	2·85	3·06	3·79	4·36	6·02

H. Försterling has also calculated values for sodium and potassium chlorides from Born's theory of space lattices.

The sp. ht. of aq. soln. of sodium chloride have been determined by J. Thomsen, A. Winkelmann, H. Teudt, J. C. G. de Marignac, and L. Demolis. The results show:

Per cent. NaCl	1·6	4·9	10·3	11·5	24·3
Temp.	18°	19°–46°	15°–90°	16°–52°	18°–20°
Sp. ht.	0·9780	0·9449	0·9120	0·8770	0·7916

L. Demolis has also measured the sp. ht. of mixtures of sodium chloride and hydroxide. According to J. Thomsen, the sp. ht. of an aq. soln. of sodium chloride at 18° with 10 mols. of water is 0·791; with 50 mols. of water, 0·931; and with 200 mols. of water per mol. of sodium chloride, 0·978. A. Jaquerod gives for the sp. ht. of soln. of potassium chloride at 16°:

Per cent. KCl	2·4	4·8	9·6	19·2	28·8
Sp. ht.	0·968	0·938	0·882	0·790	0·720

W. R. and C. E. Bousfield measured the sp. ht. of soln. of sodium and potassium chloride over the ranges 0°–13°; 13°–26°; and 26°–39°. The results show that the sp. ht. and sp. vol. of the combined water may be treated as approximately constant, and the lowering of the sp. ht. and sp. vol. of the free water on the introduction of a solute are each proportional to the percentage conc. of the solute. In dil. soln. the sp. ht. curve approximates to that of water, which has a minimum at about 25°. In conc. soln., the variation of the sp. ht. with temp. appears to follow an almost straight-line law. This behaviour is attributed to the simplification of the water by a considerable destruction of ice and steam mols. The following constants were derived: (1) for potassium chloride: the sp. ht. of the liquid solute, 1·655; the mol. ht. of the liquid solute, 123·4; (ii) for sodium chloride: sp. ht. of the liquid solute, 2·433, and the mol. ht. of the liquid solute, 142·1. The number of mols. of water combined with a mol. of solute is calculated for various dilutions. G. N. Lewis and G. E. Gibson estimate the increase of **entropy** from −273° to 25° to be 17·4 per mol. of sodium chloride, and 19·7 per mol. of potassium chloride.

The **coefficient of linear expansion** for sodium chloride is 0·00004039; and for potassium chloride, 0·00003803. The **coefficients of cubical expansion,** computed by G. P. Baxter and C. C. Wallace from sp. gr., are:

Temp.	NaCl	KCl	RbCl	CsCl
0° to 25°	0·000125	0·000084	0·000111	0·000137
25° to 50°	0·000106	—	0·000082	0·000136
50° to 70°	0·000074	0·000083	—	0·000109

The salts which produce the greatest vol. contraction on soln. in water give soln. which have the highest temp. expansion coeff.

The **thermal conductivity** of sodium chloride [20] is 0·014 to 0·016. The thermal conductivity of a 33 per cent. soln. of sodium chloride is 1·737. Just as there is a marked difference in the power of different substances to transmit light rays of different wave-length, so does the **diathermancy,** or power to transmit radiant heat of various wave-length, show marked differences. Alum and ice are almost *athermous* or opaque to radiant heat. Rock-salt is one of the most diathermous substances known. M. Melloni [21] thought that it was perfectly transparent to all kinds of radiation, and the 8 per cent. loss he observed during the passage of radiant heat through a plate of rock-salt was due to reflection from the surfaces and not to internal absorption. F. de la Provostaye and P. Desains proved that rock-salt does exhibit selective absorption, and is almost opaque to radiations from a heated piece of the same substance. H. Rubens and A. Trowbridge measured the percentage **absorption of radiant energy** by plates of rock-salt and of sylvine, 1 cm. thick, for wave-lengths from 10μ to 20·7μ; and found for 10μ rock-salt absorbed 0·3 per cent. and sylvine 1·2 per cent.; for 15μ rock-salt 15·4 and sylvine 4·6 per cent.; and for 20·7μ, rock-salt 99·4 and sylvine 41·5 per cent. Sylvine behaves like rock-salt as regards its diathermancy for heat; a plate of sylvine 26 mm. thickness

allows 76 per cent. of the incident heat to traverse it; and this is the same proportion as a plate of Stassfurt rock-salt of the same thickness. The diathermancy of both crystals does not vary with the temp. of the source, being the same for the heat emitted by a lamp as for that arising from a surface at 100°. W. L. Bragg and co-workers measured the intensity of reflexion of X-rays by the different faces of a crystal of rock-salt. E. P. Lewis and A. C. Hardy measured the reflecting power of rock-salt for the ultra-violet rays.

The **heats of formation** and the heats of soln. of the alkali chlorides[22] in water are:

	LiCl	NaCl	KCl	RbCl	CsCl
Heat of formation . .	97·9	97·7	105·7	105·94	109·86 Cals.
Heat of soln. . . .	8·421	−1·175	4·363	4·227	−2·293 Cals.

A. von Weinberg found the heat of dissociation of lithium chloride to be 193·2 Cals., of sodium chloride, 181·4 Cals.; of potassium chloride, 183·9 Cals.; of rubidium chloride, 183·8 Cals.; and of cæsium chloride, 184·2 Cals.

The **heat of solution** of the alkali chlorides in water has been determined by F. L. Haigh, M. Berthelot, J. Thomsen, V. Reichenberg, S. U. Pickering, G. Lemoine, and R. de Forcrand. The best representative values are indicated in the preceding schema. The heat of soln. of potassium chloride increases numerically with a rise of temp., being −0·513 Cal. at 3°, and −4·4 Cals. at 25°, or, according to J. Thomsen, −4·39+0·0354(θ−15) Cals.; and for sodium chloride, −1·775 Cals. at 3°, and −1·040 Cals. at 25°; or, 1·26+0·0295(θ−15) Cals. A soln. of two gram-eq. of sodium chloride in 20 gram-eq. of water when diluted by the addition of 80 gram-eq. of water absorbed 1·056 Cals. with 180 gram-eq., −1·310 Cals.; and with 380 gram-eq., −1·410 Cals. The heat of soln. of lithium chloride in ethyl alcohol is 11·74 Cals., and in methyl alcohol, 10·9 Cals. F. R. Pratt, G. Staub, and R. Scholz have studied the **heats of dilution** of soln. of potassium and sodium chlorides. J. A. Beattie and D. A. McInnes measured the free energy of dilution of soln. of lithium and sodium chlorides: M. Randall and C. S. Bisson of sodium chloride; and G. McP. Smith and co-workers for potassium and sodium chlorides.

According to M. Berthelot, heat is absorbed by the soln. of sodium chloride in water at 15°, less heat is absorbed at 76°, and heat is neither absorbed nor evolved at 100°. S. Arrhenius, A. E. Stearn, R. F. Schneider, and G. McP. Smith measured the heats of dilution of aq. soln. of sodium and potassium chlorides alone or mixed with strontium or barium chlorides; and A. J. Allmand and W. G. Polack, the free energy of dilution of soln. of sodium chloride. The heats of dilution in cals. are negative, rather greater numerically for potassium chloride than for sodium chloride.

Normality		3·2	1·6	0·8	0·4	0·2
NaCl	Water dilution	27·4	34·83	36·45	37·72	28·8
	Heat dilution	−546	−245	−70·0	−29·62	−17·64
	Water dilution	11·2	7·83	16·75	8·86	14·6
	Heat dilution	−258	−71·1	−48·44	−12·48	−10·0
KCl	Water dilution	39·0	40·0	40·0	34·95	−40·0
	Heat dilution	−781·0	289·5	−70·68	−15·0	−2·74
	Water dilution	9·4	10·0	10·0	15·0	30·0
	Heat dilution	−261·2	−103·3	−27·8	−10·0	−3·25

The existence of a measurable heat of dilution is taken to indicate the presence of complexes which are formed or decomposed by dilution. The reversible molar heats of dilution L, calculated from the relation $d \log (p/p_0)/(dt = L/RT^2$, where p and p_0 respectively denote the v.p. of the soln. and of the pure solvent at the same temp., do not agree closely with the observed results. Since L is negative, p/p_0 decreases with a rise of temp., and this agrees with an increased degree of ionization. A. A. Noyes (*vide infra*) found decreased ionization with rise of temp. Hence, the observed effects are taken to show that complexes existing in soln. are decomposed by dilution. H. Lunden estimates that the **heat of ionization** of

lithium chloride at 23° is 0·651 Cal.; of sodium chloride, 0·454 Cal.; and of potassium chloride, 0·362 Cal. The **heat of neutralization** of aq. soln. of lithium hydroxide and hydrochloric acid is 13·85 Cals.; sodium hydroxide, 13·745 Cals.; potassium hydroxide, 13·75 Cals.: or, the heat of neutralization of potassium hydroxide by hydrochloric acid is $13·60-0·05(\theta-20)$ Cals.

The **solubilities** of the alkali chlorides expressed in grams per 100 grms. of water are:

	0°	10°	20°	40°	60°	80°	100°
LiCl	67·0	41·9	78·5	90·5	103·0	115·0	127·5
NaCl	35·7	35·8	36·0	36·6	37·3	38·4	39·12
KCl	27·6	31·0	34·0	40·0	45·5	51·0	56·7
RbCl	77·0	84·4	91·1	103·5	115·5	127·2	138·9
CsCl	161·4	174·7	186·5	208·0	229·7	250·0	270·5

In addition, the solubility of sodium chloride at −15° is 32·73; at −10°, 33·49; at −5°, 34·22; at 118°, 39·8; at 140°, 42·1; at 160°, 43·6; and at 180°, 44·9. The solubility of potassium chloride at 130° is 66·0; at 147°, 70·8; at 180°, 77·5; at −9°, 23·9; and at −4·5°, 25·9. The solubility of rubidium chloride at 112·9° is 146·6; and of cæsium chloride at 119·4°, 290·0.

As early as 1819, J. L. Gay Lussac proposed to represent the solubility S of potassium chloride in water at a temp. θ by the formula $S=29·23+0·2738\theta$ grms. per 100 grms. of water. Since that time it has been customary to represent solubility curves by empirical formula of the type $S=a+b\theta+d\theta^2+\ldots$, where a, b, c, d, . . . are constants whose numerical values are calculated from the experimental data. Equations of the type $S=a+b\theta$ represent straight lines, equations with more terms represent curved lines; the solubility equation $S=a+b\theta+c\theta^2$ represents a portion of a paraboloid curve. The greater the number of terms used in the formula the greater is supposed to be the accuracy of the result.

In illustration, A. Gérardin (1865) altered J. L. Gay Lussac's formula to $S=29·23+0·2900\theta$, L. C. de Coppet to $29·33+0·3206(\theta-4)-0·000577(\theta-4)^2$, for temp. above 4°; A. E. Nordenskjöld to $\log S=1·4655-0·00379+0·000009\theta^2$ between 0° and 100°, but, according to G. J. Mulder, it is not applicable between 0° and 4°. According to A. Etard, the amount S of anhydrous salt in 100 parts of soln. between −10° and 75° is $S=20·50+0·147\theta$; and between 75° and 180°, is $S=20·50+0·0793\theta$. L. C. de Coppet's curve for the solubility of sodium chloride above 20° is $S=34·359+0·0527\theta$; J. L. Andreae's curve for the solubility of sodium chloride is $S=35·63+0·007889(\theta-4)+0·0003113(\theta-4)^2$; G. Karsten's, $S=26·519+0·0169559\theta+0·000090161 5\theta^2$. H. Kopp's, $S=35·48+0·024748\theta+0·0001000\theta^2+0·000002655 55\theta^3$; A. E. Nordenskjöld's, $\log S=0·448+0·000105\theta+0·00000319\theta^2$; C. A. Raupenstrauch's, $S=39·575+0·0088588(\theta-0·5)+0·00027955(\theta-0·5)^2$, and D. I. Mendeléeff's curve for the number of grams of sodium chloride in 100 grms. of water, at θ° between 0° and 108°, is $S=35·7+0·024\theta+0·002\theta^2$—below 0°, the equation is inapplicable because of the formation of the dihydrate. The percentage composition S of sat. soln. of sodium chloride at θ° is represented by G. Karsten [23] by the expression $S=26·519-0·0169559\theta+0·0000901615\theta^2$.

The equations are sometimes useful, but it must be borne in mind that the formulæ are equations of continuous curves, whereas actual solubility curves are not usually continuous except over limited ranges of temp. determined by the stability of particular phases—*e.g.* hydrates. The effect of *pressure* on the solubility of sodium chloride has been previously indicated. C. Möller showed in 1862 that the solubility is increased by 20 and by 40 atm. press. The thermal expansion of salt soln. was also found by G. C. Schmidt to be more regular than with water. W. C. Röntgen and J. Schneider, and V. Schumann, have measured the compressibility of soln. of potassium and sodium chlorides.

The solubility of each chloride is depressed in the presence of another salt with a like ion—for instance, the solubility of sodium chloride is depressed by increasing proportions of *ammonium* or *potassium chlorides*, or by *sodium carbonate*, *hydroxide*, or *nitrate*. Similar results obtain with potassium chloride, in the presence of

ammonium, magnesium, or sodium chloride, or by *potassium bromide, hydroxide*, or *nitrate*. The effect of salts with no common ion is often to raise the solubility. Thus, C. J. B. Karsten [24] found the solubility of sodium chloride in water at 15° rises to 39·19 in the presence of 38·53 grms. of potassium nitrate. This effect is due to the formation of complexes or to chemical reaction. With Karsten's mixture there is a balanced reaction: $NaCl+KNO_3 \rightleftharpoons KCl+NaNO_3$. When a mixed soln. of sodium chloride and potassium sulphate is cooled down to between 3° and 7°, crystals of what van't Hoff calls the *reciproke Salspaar*—pair of reciprocal salts—sodium sulphate and potassium chloride separate. As a rule the solubility of sodium chloride in soln. of non-electrolytes or feeble electrolytes is diminished in such a way that if S_0 denotes the solubility of the non-electrolyte in water; S, the solubility of the salt in the soln.; and N, the normality of the soln., then $(S_0-S)/NS_0$ is a constant. J. N. Brönsted measured the solubility of potassium chloride in soln. of potassium hydroxide of different conc. C. Chorower studied the mutual action of alkali chlorides and hydroxides. F. A. H. Schreinemakers and G. M. A. Kayser found the solubility of lithium chloride is much depressed in the presence of the sulphate.

Soln. of various gases in brine and other salt soln. have been investigated from this point of view.[25] For example, E. G. Kumpf, W. L. Goodwin, and C. A. Kohn and F. O'Brien have investigated the system $H_2O-NaCl-Cl_2$—*vide* chlorine; C. J. J. Fox, the solubility of sulphur dioxide in salt soln.; R. Abegg and H. Riesenfeld, D. P. Konowaloff, and A. Joannis the solubility of ammonia in salt soln.; and C. G. MacArthur the solubilities of oxygen in an aq. soln. of the alkali chlorides. For $\frac{1}{8}N$-soln. of the alkali chlorides, the solubility of oxygen in c.c. per 1000 c.c. of the salt soln. at 25° when water unity has the sp. gr. 1000 at 25° and dissolves 5·78 c.c. of oxygen per litre:

	LiCl	NaCl	KCl	RbCl	CsCl	NH_4Cl
Sp. gr. . . .	1·0004	1·0022	1·0030	1·0094	1·0140	1·0015
Oxygen c.c. . .	5·63	5·52	5·52	5·65	5·67	2·31

The decrease in solubility does not proceed regularly with a decrease in the mol. wt. from cæsium to rubidium. The solubility of oxygen decreases as the conc. of the salt soln. increases. Thus, for $\frac{1}{2}N$-sodium chloride soln. the solubility is 5·30 c.c. per litre; for N-soln., 4·20; for $2N$-soln., 3·05; for $4N$-soln., 1·62. The decrease with ammonium chloride is very great, being 0·07 with N-soln. The decrease is attributed to the fixation of water by the salt or the ions of the salt, or both, a question previously discussed.

H. C. Sorby showed that while the solubility of sodium chloride is raised by press., that of ammonium chloride is decreased by press., and that the soln. of the former is accompanied by a decrease in volume, while the soln. of the latter is attended by an increase in volume. F. Braun made analogous observations. E. Cohen [26] and co-workers have made careful measurements of the effects of press. on the solubility of sodium chloride. At 24·05°, 100 grms. of water dissolve 35·90 grms. of this salt at one atm. press.; 36·25 grms. at 250 atm.; 36·55 grms. at 500 atm.; 37·02 grms. at 1000 atm.; and 37·36 grms. at 1500 atm. press.; or, the solubility S of sodium chloride at 24·05°, and a press. p between 1 and 1500 atm. is $S=35{\cdot}898+0{\cdot}001647p-0{\cdot}0000003268p^2$ grms. per 100 grms. of water.

C. J. B. Karsten, A. Fock, C. J. Mulder, A. Winkelmann, K. van Hauer, F. Rüdorff, and P. P. Fedotéeff have measured the solubility of sodium or potassium chloride in soln. of *ammonium chloride*, and in soln. of sodium bicarbonate; C. J. B. Karsten, A. Winkelmann, F. Margueritte, F. Rüdorff, and J. Hannaman, in *ammonium nitrate;* F. Rüdorff, in *ammonium sulphate;* C. J. B. Karsten, G. J. Mulder, H Kopp, A. Levol, J. H. van't Hoff and W. Meyerhoffer, and H. Precht and B. Wittgen, in soln. of *sodium* or *potassium sulphate;* or *magnesium chloride;* M. Berthelot, R. Engel, and F. Winteler in *aq. sodium hydroxide;* C. Touren, G. Bödlander, W. W. J. Nicol, C. A. Soch, A. Winkelmann, H. Kopp, G. J. Mulder, R. W. Page, and A. D. Keightly and C. J. B. Karsten, in soln. of *sodium*

or *potassium nitrate;* A. Fock and K. van Hauer in soln. of *sodium* or *potassium bromide;* J. H. Gladstone and F. Margueritte with *potassium chlorate;* C. J. B. Karsten in soln. of *barium chloride;* K. van Hauer and A. Etard in soln. of *potassium or sodium iodide;* and H. Precht and B. Wittzen. C. A. Soch. A. Etard. A. Winkelmann, C. J. B. Karsten, F. Rüdorff, and W. W. J. Nicol. of sodium and potassium chloride in the presence of one another.[27]

The solubilities of sodium and potassium chlorides in soln. of *hydrochloric acid*[28] are depressed in a similar manner; thus, the solubilities of sodium and potassium chlorides represented by the number of grams per 100 c.c. of soln., are, at 0°,

HCl	1·42	2·41	4·05	8·29	12·40	14·95	23·88
KCl	22·69	20·84	17·71	11·93	7·46	5·60	1·49
HCl	1·859	3·38	5·49	11·20	20·54	94·77	120·6
NaCl	23·4	25·7	22·6	13·7	3·6	2·01	1·6

Similarly, R. Engel found that with 8·2, 24·1, 29·5 grms. of hydrogen chloride, the soln. can dissolve respectively 41·4, 28·5, 24·6 grms. of lithium chloride. R. Engel[29] noticed empirically that with barium, strontium, and other chlorides the solubility diminishes in the presence of hydrochloric acid by a quantity which corresponds with an eq. of chloride for each eq. of hydrochloric acid added; or, in other words, the sum of the eq. of the chloride and acid remains constant. The sum of the eq. at first diminished slightly and then increased. This rule did not hold good after the solubility had fallen less than one-fourth its value in water; with ammonium chloride, on the contrary, the sum of the eq. steadily and gradually increased. G. Jeannel further found that Engel's rule is not applicable to potassium chloride and hydrochloric acid unless the water is taken into account, when the sum of the eq. of the three substances remains constant; and generally, excepting for very slight deviations, G. Jeannel found that the solubility of the chlorides in water in the presence of hydrochloric acid varies so that the sum of the eq. of salt, acid, and water in soln. are nearly constant at the same temp., whatever be the nature of the chloride. The addition of *mercuric chloride* raises the solubility in consequence of the formation of the double salt, $2HgCl_2.NaCl$.

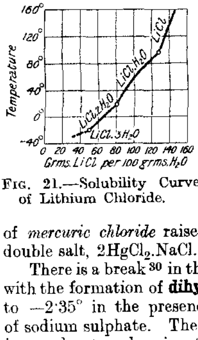

FIG. 21.—Solubility Curve of Lithium Chloride.

There is a break[30] in the solubility curve of sodium chloride at 0·15° corresponding with the formation of **dihydrated sodium chloride,** $NaCl.2H_2O$; this point is lowered to −2·35° in the presence of potassium chloride, and to −2·85 in the presence of sodium sulphate. The eutectic or cryohydrate temp. for the system $NaCl.2H_2O$, ice, and sat. soln., is at −21·2°; and the eutectic mixture has 28·9 grms. of sodium chloride; and with potassium chloride the eutectic temp. is −10·9° for soln. containing 39 grms. of salt. The eutectic $KCl+18H_2O$ is not a definite compound.

The work of A. Bogorodsky[31] shows that lithium chloride forms three hydrates—(i) needle-like crystals of **trihydrated lithium chloride,** $LiCl.3H_2O$; this passes into (ii) **dihydrated lithium chloride,** $LiCl.2H_2O$, at −15°; the latter passes into (iii) **monohydrated lithium chloride,** $LiCl.H_2O$, at 12·5° (perhaps 21·5°); and the latter, in turn. into the anhydrous salt at 98°. The last three compounds crystallize in cubes or octohedra in the cubic system. A supersaturated soln. of the dihydrate in 98 per cent. alcohol is said to deposit the hydrate $2LiCl.3H_2O$. These hydrates have not been closely investigated; the solubility curve is supposed to be that indicated more or less diagrammatically in Fig. 21.

The solubilities of the alkali chlorides in soln. of *ethyl alcohol* decreases with increasing proportions of alcohol, and become very small in absolute alcohol.

According to C. A. L. de Bruyn, 100 grms. of absolute ethyl alcohol dissolve 0·034 grm. of potassium chloride at 18·5°, and 0·065 grm. of sodium chloride. A mixture of equal parts of 96 per cent. alcohol, and 98 per cent. ether, says A. Mayer, dissolves 0·011 grm. of sodium chloride. The number of grams of sodium chloride which can be dissolved by a 100 c.c. of aq. alcohol of different conc. is as follows:

Ethyl alcohol (13°) .	11·81	15·99	24·95	40·33	57·91	72·26
NaCl	23·26	20·81	16·23	9·13	3·47	0·50
Sp. gr. . . .	1·1348	1·1144	1·0698	0·9880	0·9075	0·8400

Similarly, with potassium chloride:

Ethyl alcohol (14·5°) .	2·79	10·56	20·66	40·42	48·73	68·63
KCl	26·85	20·56	14·27	6·35	3·82	0·30
Sp. gr. . . .	1·1542	1·0545	1·0545	0·9695	0·9315	0·8448

The solubility increases with temp. For example, with ethyl alcohol, of sp. gr. 0·9282, that is, aq. alcohol with 54 per cent. by weight of alcohol, dissolves per 100 grms. of solvent at

	4°	10°	23°	32°	44°	51°	60°
Grms. NaCl . . .	10·9	11·1	11·9	12·3	13·1	13·8	14·1

The solubility of potassium chloride in ethyl alcohol of sp. gr. 0·939 rises from 4·0 at 0° to 11·8 at 60°. Similar results are obtained with other mixtures of alcohol and water. According to C. A. L. de Bruyn,[32] 100 grms. of 98 per cent. methyl alcohol dissolve 1·22 grms. of sodium chloride, and 14 grms. dissolve in 40 per cent. methyl alcohol; 100 grms. of *propyl alcohol* of sp. gr. 0·816 dissolve 0·033 grm. of sodium chloride at room temp., while potassium chloride is almost insoluble in this menstruum, and luminescence occurs when soln. of hydrogen chloride in propyl alcohol are treated with potash lye.[33] At 17°, 100 mols. of *acetic ether* dissolve 0·31 mol. of sodium chloride, and at 40°, 0·037 mol.

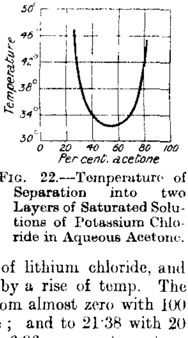

FIG. 22.—Temperature of Separation into two Layers of Saturated Solutions of Potassium Chloride in Aqueous Acetone.

The solubility of sodium chloride in aq. *acetone* at 20° falls to 27·18 with 10 c.c. of acetone per 100 c.c. of solvent to 0·25 with 90 c.c. of acetone per 100 c.c. of solvent; at 0°, 100 grms. of acetone dissolve 4·6 grms. of lithium chloride, and at 58°, 2·14 grms., so that the solubility is diminished by a rise of temp. The solubility of potassium in aq. soln. of acetone increases from almost zero with 100 per cent. acetone at 20° to 8·46 with 50 per cent. acetone; and to 21·38 with 20 per cent. acetone. At 30°, 100 grms. of a soln. with 6·96 per cent. acetone carries 23·42 per cent. potassium chloride and the remainder is water; 8·06 per cent. of this salt is present in a soln. with 45·98 per cent. acetone; and 0·13 per cent. of this salt in a soln. with 89·88 per cent. of acetone. At 40°, a soln. with 15·75 per cent. acetone carries 21·28 per cent. of potassium chloride; and with 79·34 per cent. of acetone there is 0·58 per cent. of potassium chloride. At 40°, therefore, for conc. of acetone between 20 and 80 per cent., the sat. soln. separates into two layers; the upper layer has 55·2 per cent. water, 31·82 acetone, and 12·99 KCl, when the lower layer has 28·14 per cent. water, 69·42 acetone, and 2·44 KCl. Similarly, when the upper layer has water, acetone, and potassium chloride in the respective ratio 46·49, 45·34, and 8·17; the lower layer has 38·68, 56·17, and 5·25. The *separation into two layers with sat. soln. of potassium chloride* containing 26 per cent. acetone, occurs at 46·5° and the temp. of separation with other proportions of acetone is indicated in Fig. 22. C. E. Linebarger (1892) and J. E. Snell (1898)[34] found the phenomenon also occurs with the chlorides of lithium, ammonium, sodium, rubidium, calcium, strontium, cobalt, and many other radicles; also with bromides, sulphates, cyanides, and numerous other salts with aq. acetone,

in aq. propyl alcohol, and with methyl alcohol C. E. Linebarger observed the phenomenon only with potassium carbonate. The phenomenon, indeed, was first mentioned by Raymond Lully in the thirteenth century; for, when preparing conc. alcohol, he noticed that the addition of potassium carbonate to aq. soln. of ethyl alcohol caused the liquid to separate into two layers. Centuries later. R. Brandes, H. Schiff, J. Traube, and O. Neuberg, and C. E. Linebarger added many other examples. J. F. Snell studied the condition of the formation of two liquid phases in a three component system—water, acetone, and potassium chloride.

Lithium chloride is fairly soluble in many organic fluids, and in some cases much heat is developed, and compounds are formed.[35] *E.g.* the compounds $LiCl.3CH_3OH$; $LiCl.4C_2H_5OH$ have been isolated. According to H. E. Patten and W. R. Mott, 100 grms. of a sat. soln. of lithium chloride in water at 25° contains 45·0 per cent. of the salt; in *ethyl alcohol*, 2·475 grms. of the salt; in *propyl alcohol*, 3·720 grms.; in *butyl alcohol*, 9·56 grms.; in *amyl alcohol*, 8·25 grms.; in *allyl alcohol*, 4·20 grms.; and in *phenol*, 1·89 grms. L. W. Winkler found lithium chloride to be readily soluble in primary butyl alcohol, while the chlorides of sodium and potassium are very sparingly soluble. According to G. Lemoine, the solubility of lithium chloride in the alcohols decreases proportionally with the mol. wt. of the alcohol. F. A. Gooch says that 10 c.c. of amyl alcohol dissolve 0·66 grms. of lithium chloride, 0·0041 grm. of sodium chloride, 0·0051 grm. of potassium chloride, and less than 0·009 grm. of rubidium and cæsium chloride. L. N. Andrews and C. Ende have shown that lithium chloride has a tendency to polymerize when dissolved in alcohol and other organic solvents; H. C. Jones and co-workers have also shown that there is a tendency to form complexes between the lithium salt and the organic solvent; while E. W. Washburn and E. W. McInnes calculate that in a $\frac{1}{2}N$-aq. soln. of lithium chloride, each mol. of the solute is hydrated with 18 mols. of the solvent. F. G. Donnan and W. E. Garner have studied the *distribution ratio of lithium chloride between* amyl alcohol and water. $[LiCl]_{Am} \div [LiCl]_{Aq} = 0{\cdot}0273$.

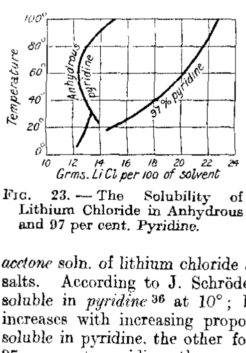

FIG. 23. — The Solubility of Lithium Chloride in Anhydrous and 97 per cent. Pyridine.

S. W. Serkoff has studied the properties of *acetone* soln. of lithium chloride and found evidence of the formation of complex salts. According to J. Schröder, potassium or sodium chloride is not perceptibly soluble in *pyridine*[36] at 10°; but in aq. soln. of this menstruum, the solubility increases with increasing proportions of water. Thus, while lithium chloride is soluble in pyridine, the other four alkali chlorides are insoluble in anhydrous and 97 per cent. pyridine, they are very slightly soluble in 95 per cent. pyridine, and still more so in 93 per cent. pyridine. The solubilities of lithium chloride in anhydrous and in 97 per cent. pyridine soln. at different temp. are shown in the diagram, Fig. 23. The curious break in the curve with anhydrous pyridine is supposed to be due to the fact that below 28° the soln. contains $LiCl.2C_5H_5N$, and above 28°, $LiCl.C_5H_5N$. The table shows that at 20°, 100 grms. of anhydrous pyridine dissolve 13·39 grms. of lithium chloride, and 100 grms. of the 97 per cent. pyridine (97 vols. anhydrous pyridine, 3 vols. water) at 22° dissolve 14·31 grms. of lithium chloride. According to J. Schröder, potassium chloride is not appreciably soluble in aq. pyridine, but it dissolves in aq. pyridine, and this the more the greater the proportion of water in the solvent. The very sparing solubilities of potassium and sodium chlorides in amyl alcohol, and in pyridine have been used for the analytical separation of lithium chloride from the other alkali chlorides in F. A. Gooch's and L. Kahlenberg's processes[37] respectively.

With *glycerol*[38] of sp. gr. 1·2555 (25°) the solubility of sodium chloride at 25° falls from 31·93 to 29·31 grms. per 100 c.c. of soln. with 13·21 per cent. glycerol as

solvent; and to 9·78 grms. per 100 c.c. of solvent with 100 per cent. glycerol. The corresponding numbers for potassium chloride are 28·61 grms. per 100 c.c. of soln. with 13·28 per cent. glycerol, and 8·25 grms. with 100 per cent. glycerol. At 15°, 100 grms. of glycerol dissolve 11·0 grms. of lithium chloride, and 31·7 grms. at 14·8°. According to W. F. O. de Coninck, a sat. soln. of *ethyl glycol*, $C_2H_4(OH)_2H_2O$, at about 15°, has 11·0 per cent. of lithium chloride; and 37·1 per cent. of sodium chloride; while P. Walden found that at 25°, 100 grms. of *furfural*, $C_4H_3O.COH$, dissolve 0·085 grm. of potassium chloride, and A. Köhler states that a sat. soln. at 31·25° contains 11·33 per cent. of potassium chloride, and 62·28 per cent. of *sugar*; or 62·17 per cent. of sugar and 11·13 per cent. of sodium chloride. M. Stuckgold found that a litre of ethyl urethane at 60° dissolved 0·023 mol. of sodium chloride, 0·014 of potassium chloride. Potassium chloride does not dissolve in anhydrous and *liquid hydrogen chloride*; it dissolves in soln. of *antimony trichloride*,[39] and is said to form a complex $23KCl.10SbCl_3$. Sodium chloride dissolves in anhydrous *liquid ammonia*, but not in *liquid carbon dioxide*.

According to J. L. Andreae, a small contraction occurs when sodium chloride is dissolved in water, such that the **specific gravity,** S, of a sat. soln. which has a sp. gr. S at $\theta°$, is, at $\theta°$, $S=0·000434(\theta_1-\theta)+0·00000017(\theta_1-\theta)^2$; D. I. Mendeléeff's formula is $S=0·99916+0·007117p+0·0000214p^2$ (water at 4° unity). According to G. T. Gerlach,[40] the sp. gr. at 15° of soln. of sodium and potassium chlorides are:

Per cent. of salt . .	1	5	10	15	20	24
Sp. gr. NaCl (15°) .	1·0073	1·0362	1·0733	1·1115	1·1511	1·1840
KCl (15°) . . .	1·0065	1·0325	1·0658	1·004	1·1361	1·1657

and 1·200098 with a 26 per cent. soln. of sodium chloride, and 1·1723 with a 24·9 per cent. soln. of potassium chloride. W. H. Green gives for soln. of lithium chloride of normality N, at 18°/4°

N	0·1	0·5	1·0	5·0	10·0	12·5
Sp. gr. LiCl (18°) . .	1·00114	1·01082	1·03400	1·11015	1·21575	1·2686

R. Hosking, G. T. Gerlach, and G. Lemoine's values for the sp. gr. of soln. of lithium chloride at 15°, referred to water at 4° for soln. with C mols. of the salt per litre are:

C	0·00654	0·1030	0·5230	1·0125	2·937	5·02	10·71
Sp. gr. . . .	0·9992	1·0016	1·0115	1·0234	1·0665	1·1107	1·2319

M. le Blanc and P. Rohland's, W. Biltz's, and F. Fouqué's values for the sp. gr. of soln. of rubidium chloride run from 1·0502 to 1·0805 at room temp. when the conc. rises from 6·64 to 10·59 per cent. The sp. gr. of a 0·33 per cent. soln. of cæsium chloride is 1·0021 at 0°, and 1·0018 at 11°. J. A. Groshans noted that solid sodium compounds have a greater sp. gr. than the corresponding potassium compounds, and with aq. soln., with an equal number of mols. per unit vol., the sp. gr. of the potassium soln. is greater than that of the sodium compound. F. L. Haigh's values for the sp. gr. of N-soln. at 20°/4° are:

	LiCl	NaCl	KCl	RbCl	CsCl
Sp. gr.	1·02237	1·03866	1·04443	1·085405	1·125815

In general, the temp. coeff. of normal soln., of the chlorides of potassium, rubidium, or cæsium are identical within the limits of experimental error; but sodium chloride soln. expand a little faster; and lithium salt soln. a little less rapidly. F. L. Haigh measured the expansion of normal soln. of the alkali chlorides at between 20° and 0°, and between 20° and 50°:

	LiCl	NaCl	KCl	RbCl	CsCl
20°–0°	–27·1	–42·0	–38·5	–38·7	–38·9
20°–10°	–18·0	–25·4	–23·5	–23·7	23·2
20°–30°	27·0	32·7	32·7	31·1	31·4
20°–40°	61·1	71·4	71·4	69·4	69·3
20°–50°	101·2	116·2	116·2	113·0	112·4

J. L. Andreae represents the volume v of a soln. at $\theta°$ by $v=v_1[1+0·000444(\theta-\theta_1)+0·000000978(\theta-\theta_1)^2]$, where v_1 represents the volume at $\theta_1°$. K. Zepernick and G. Tammann represent the volume v of a soln. containing 2·78 grms. of sodium chloride per 100 grms. of water at $\theta°$, by $v=1·0524+0·000840(\theta-100)+0·0000020(\theta-110)^2$; and when the soln. contains 12·21 grms., $v=1·0555+0·000802(\theta-110)$. For soln. with 3·94 grms. of potassium chloride per 100 c.c., $v=1·0536+0·000728(\theta-110)+0·0000042(\theta-110)^2$; and with 15·76 grms., $v=1·0528+0·000758(\theta-110)+0·0000011(\theta-100)^2$. N. A. Tschernay gives for the volume v of a soln. at $\theta°$: lithium chloride, $LiCl+50H_2O$, $v=1+0·0_4652\theta+0·0_54355\theta^2$; sodium chloride, $NaCl+50H_2O$, $v=1+0·0_31457+0·0_53758\theta^2$; $NaCl+100H_2O$, $v=1+0·0_4602\theta+0·0_54825\theta^2$; potassium chloride, $KCl+50H_2O$, $v=1+0·0_31239\theta+0·0_53611\theta^2$; $KCl+100H_2O$, $v=1+0·0_4590\theta+0·0_54407\theta^2$; and for rubidium chloride, $RbCl+50H_2O$, $v=1+0·0_31267\theta+0·0_53716\theta^2$. G. P. Baxter has measured the sp. gr. of soln. of the five alkali chlorides and compared the observed mol. vol. of the solid with those computed from the at. vol. of the elements and with the mol. vol. of the salts in soln. F. Kohlrausch and W. Hallwachs have measured the sp. gr. of very dil. soln. of salt. J. E. Ekman found empirically that the percentage amount of sodium chloride in sea water of sp. gr. 1·0166 is 130×0·0166=2·158 per cent. of sodium chloride. S. Lussana found the temp. θ of maximum density of 0·50 and 1·44 per cent. aq. soln. of sodium chloride can be represented respectively by $\theta=3·35-0·0177(p-1)$ and $\theta=0·77-0·0110(p-1)$.

The **rate of solution** of the different faces of a crystal of rock-salt is slightly *different, being rather faster on the octohedral face than on a cubic face, and* intermediate between these two rates on the dodecahedral face.[41] A. Ritzel has shown *that in the absence of urea, the octohedral faces dissolve fastest, and in the* presence of urea, the cubic faces. W. Poppe found that with 0·5 and 1·0 per cent. under-sat. soln., each crystal face dissolves at a characteristic rate, but with a 2 per cent. under-sat. soln., all the faces dissolve at approximately the same rate. The solubility of cubic and octohedral crystals per 100 c.c. of water at the end of a given time is:

Grams urea	0	5	13	18	23	28
Cubic crystals	5·451	5·240	4·874	4·733	4·668	4·559
Octohedral crystals	5·453	5·240	4·868	4·725	4·648	4·650

W. Schnorr has also made a study of the dissolution of sodium chloride in soln. of urea.

The **boiling points of aqueous solutions** of sodium chloride[42] containing per 100 grms. of water,

Grams of NaCl	7·6	11·0	14·9	18·8	24·0	26·0	28·7
B.p.	102·2°	103·0°	104·2°	106·1°	107·7°	108·7°	109·5°

Similarly with potassium chloride,

Grams of KCl	9·2	16·7	23·4	29·9	36·2	48·4	57·4
B.p.	101°	102°	103°	104°	105°	107°	108·5°

A sat. soln. of lithium chloride boils at 168°. The b.p.[43] of lithium chloride soln. was raised 0·130° by the addition of 0·135 mol. of the salt to 1000 grms. of water, and 1·743°, with 1·624 mols. The effect *this* salt has *on the* b. and f.p. *of* water is greater than would be expected if the salt were completely ionized. This is *attributed to the formation of hydrates which makes the ratio mols. of solute:* mols. of solvent assume a higher value than that calculated from the analysis of soln. The curve *relating the mol. rise of the* b.p. of soln. of the *alkali* chlorides with conc. shows a minimum which is least with the chlorides with the greatest mol. wt.; with a soln. containing 0·0409 mol. of rubidium chloride in 1000 grms. of water, the b.p. rises 0·039°; with 0·3458 mol., 0·313°; and with 0·9419 mol., 0·860°. The corresponding mol. rises in the b.p. are 0·95°, 0·905°, and 0·913°.[44]

The **freezing points of aqueous solutions** of sodium chloride[45] are represented by C. J. B. Karsten's formula $0·00222442p^2-0·7663855p$, where p denotes the percentage composition of the soln. According to C. Blagden and C. M. Despretz, the lowering of the f.p. of a soln. is proportional to the quantity of salt dissolved in a given volume of the solvent; but, according to L. C. de Coppet, this is neither the case for anhydrous sodium chloride, nor for the dihydrate, $NaCl.2H_2O$. With soln. containing 5 grms. of sodium chloride per 100 grms. of water, the f.p. is lowered 0·580° per gram NaCl, or 0·348° per gram $NaCl.2H_2O$; the corresponding numbers for soln. with 31·34 grms. of salt are 0·775° per gram NaCl, and 0·378° per gram $NaCl.2H_2O$; if N denotes the number of mols. of sodium chloride per 1000 grms. of water, the lowering of the f.p. of soln. less than $\frac{1}{10}N$-NaCl can be represented by $3·5534N-1·006N^2$. For a soln. with 0·0746 grm. or 0·001 mol. of potassium chloride in 100 grms. of water, the lowering of the f.p. corresponds with a substance with a mol. wt. 36, that is about half the mol. wt. of potassium chloride. In dil. soln. therefore this salt is assumed to be completely ionized, and the percentage ionization of other soln. can be computed from their mol. wt. calculated from the lowering of their f.p. The f.p. of a soln. containing 0·2172 grm. of potassium chloride per 100 c.c. is −0·1031°; and one containing 24·39 grms. per 100 c.c., −10·61°. The lowering of the f.p.[46] for soln. between 0·1 and $0·02N$-KCl can be represented by $3·5605N-0·98196N^2$; and for soln. of lithium chloride the number of mols. of the salt in 1000 grms. of water between $N=0·2938$ and 0·02503 by $3·6116N-0·88570N^2$. For soln. of lithium chloride with $N=0·5136$, the f.p. was lowered 1·853°, and for $N=07939$, 2·945°. With a soln. of 0·1095 mol. of rubidium chloride in 1000 grms. of water, the f.p. was lowered 1·853°, and for $N=0·7939$, 2·945°. With a soln. of 0·1095 mol. of rubidium chloride in 1000 grms. of water, the f.p. was lowered 0·379°; and with 0·7608 mol., 2·483°. With a soln. of 0·0952 mol. of cæsium chloride, the f.p. was lowered 0·338°; and with 0·6930 mol., 2·240°. The higher the at. wt. of the alkali chloride the more closely do the results agree with the ionization calculated by W. Ostwald's law of mass action.

The **vapour pressure of aqueous solutions** has been measured by F. M. Raoult,[47] A. Smits, C. Dieterici, and G. Tammann. A soln. with 0·25793 grm. of sodium chloride per 100 c.c. at 0° was reduced 0·007197 mm. of mercury; and a soln. of 19·657 grms., 0·53442 mm. Similarly, with a soln. of 2·0 grms. of potassium chloride per 100 c.c. the vap. press. was lowered 3·033 mm., and with a soln. of 15 grms., 3·310 mm. A vap. press. of a soln. containing 4·27 grms. of lithium chloride in 100 grms. of water at 100° was lowered 25·7 mm. of mercury; with 13·86 grms. of rubidium chloride, 29·1 mm.; with 28·35 grms. of rubidium chloride, 59·2 mm.; and with 28·92 grms. of cæsium chloride, 45·1 mm. W. L. Badger and E. M. Baker measured the vap. press. of soln. of sodium chloride at different conc. and temp., and B. F. Lovelace, J. C. W. Frazer, and V. B. Sease, of soln. of potassium chloride at 20°. H. von Fehling noted that a sat. soln. of sodium chloride attracts moisture from the atm.

The **viscosity** of a normal soln. of sodium chloride is 1·093; and of potassium chloride, 0·978—water at 25° unity;[48] and for N-, $\frac{1}{2}N$-, $\frac{1}{4}N$-, and $\frac{1}{8}N$-soln. of sodium chloride J. Wagner gave the respective viscosities: 1·0073, 1·0471, 1·0239, and 1·0126; and of potassium chloride, 0·9872, 0·9874, 0·9903, and 0·9928. The viscosity of lithium chloride soln. containing C mols. of the salt per litre at 15° is:

C . . .	10·71	5·02	2·937	1·0125	0·5203	0·1030	0·00654
Viscosity . .	0·0805	0·02331	0·01718	0·01308	0·01220	0·01229	0·01144

According to J. Wagner, the viscosity of normal soln. of rubidium chloride at 25° is 0·9846; and of cæsium chloride, 0·9775, under similar conditions. W. H. Green measured the viscosity and fluidity of aq. soln. of lithium chloride at 17·92° and 25°; he found at 25° for $0·6175N$, $5·325N$, and $12·345N$-soln. the respective values 0·009724, 0·019319, and 0·09589 when the value for water is 0·008955. R. Cohen measured the effect of press. on the viscosity of soln. of

sodium and ammonium chlorides of different conc. The results with soln. of sodium chloride of different percentage composition are indicated in Fig. 24. The dotted curves refer to a temp. of 2°, the continuous curves, 14·5°. The results for water alone are marked 0 per cent. The more dil. the soln. the more apparent is the anomalous behaviour of water. There is a definite temp. for soln. between 5 and 10 per cent. at which the influence of press. of 600 atm. is zero. F. Körber represented the effect of press. p on the viscosity η of 0·01N-soln. of the alkali halides at 19·18° *in terms of* $d\eta/\eta dp$, as indicated in Table XIX.

TABLE XIX.—EFFECT OF PRESSURE ON THE VISCOSITIES OF SOLUTIONS OF THE ALKALI HALIDES.

Press.	HCl	LiCl	NaCl	KCl	NaBr	KBr	NaI	KI
1	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000
500	−0·0274	−0·0240	−0·0148	−0·0170	−0·0097	−0·0113	−0·0019	−0·0039
1000	−0·0490	−0·0374	−0·0194	−0·0246	−0·0114	−0·0150	+0·0062	−0·0012
1500	−0·0630	−0·0442	−0·0190	−0·0238	−0·0041	−0·0086	+0·0214	+0·0148
2000	−0·0720	−0·0473	−0·0103	−0·0169	−0·0086	+0·0031	+0·0404	+0·0326
2500	−0·0773	−0·0492	+0·0024	−0·0055	+0·0255	+0·0173	+0·0616	+0·0523
3000	−0·0795	−0·0496	+0·0164	+0·0066	+0·0456	+0·0347	+0·0862	+0·0742

The **diffusion coefficient,** k, of sodium and lithium chlorides per cm. per sq. cm. per day, is for soln. of normality N,

N	2	1	0·5	0·2	0·05	0·01
k NaCl	1·109	1·078	1·065	1·069	—	—
k LiCl	0·928	0·920	0·919	0·929	0·971	1·000

and for potassium chloride soln. of normality 2·95N, 1·60; 0·9N, 1·52; 0·1N, 1·38; and 0·02N, 1·36. F. G. Donnan and co-workers have studied [49] the equilibrium in aq. soln. of two salts at either side of a membrane impermeable to one of the salts—*e.g.* a diaphragm of copper ferrocyanide with an aq. soln. of potassium chloride on both sides and of potassium ferrocyanide on one side.

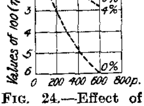

FIG. 24.—Effect of Pressure on the Viscosity of NaCl-solutions.

R. Rother [50] found the **surface tension** of aq. soln. of *sodium chloride to be* 7·357+0·1566x milligrms. per mm., where 7·357 represents the surface tension of water in the same units, and x the number of gram eq. of the salt in 100 eq. (900 grms.) of water. Otherwise expressed, the surface tension of an aq. soln. of sodium chloride containing N-mols. of salt per litre is 72·17+1·382N dynes per cm., where 72·17 represents the surface tension of water in the same units. *According to* W. Grabowsky, *the surface tension of a* 9·47 per cent. soln. of potassium chloride at 10° is 75·97 dynes per cm., and at 30°, 73·05 dynes per cm.; for a 18·27 per cent. soln. at 10° and 30°, respectively, 78·14 and 75·13 dynes per cm.; and for a 23·32 per cent. soln., at 10° and 30°, respectively, 79·63 and 76·75 dynes per cm. For a 10·24 per cent. soln. of sodium chloride at 10° and 30°, respectively, 77·27 and 74·22 dynes per cm.; for a 18·71 per cent. soln. respectively, 80·26 and 75·55 dynes per cm.; and for a 26·24 per cent. soln., respectively, 83·96 and 80·95 dynes per cm.

A. Heydweiller [51] sought to measure the cohesion between a solute and solvent by means of the volume changes which occur on soln. If m be the mass of an ion, and u its mobility, the product kmu is called the *Ionenmodulus*, and k is a constant 0·00112 for univalent ions, and 0·06372 for bivalent ions. The modulus was calculated in various ways, and the result was considered to represent the cohesion

between water and compounds of the elements. The product *mu* may be regarded as representing the characteristic electric charge of an ion. Cohesion is therefore assumed to be proportional to the electric charges of the ions. In chemical compounds, the negative ion seems to play the principal part in determining cohesion. This is shown by plotting the specific cohesion of the molten sodium and potassium halides against the charges of the negative ions (where the hydrogen charge is regarded as +4·84). The specific cohesion *c* was measured by S. Motylewsky, and the calculated values were obtained from $c=630/(e+60)$, where *e* denotes the charge of the negative ion. In a given family of salts the sp. gr. varies approximately as the sq. root of the atomic charge, so that the observed sp. gr. *D* corresponds with the values calculated from the equation $D=1·5+0·022\sqrt{2ee'}$—calcium iodide does not give good results, but this may be because the observed sp. gr. is inaccurate.

	NaCl	KCl	NaBr	KBr	NaI	KI
e	35·2	35·2	82·8	82·8	129	129
c obs.	6·63	6·55	4·44	4·41	3·53	3·44
c calc.	—	6·59	—	4·43	—	3·44

F. E. Bartell and O. E. Madison [52] have studied the **osmosis** of acidic and alkaline 0·05*N*-soln. of potassium, sodium, and lithium chlorides through goldbeaters' skin membranes.

The **refractive indices**, μ, of sodium and potassium chlorides,[53] for visible rays of wave-length 0·768 to 0·441, are:

Wave-length	768	627	560	508	486	467	441
μ NaCl	1·53671	1·5421	1·5463	1·5509	1·5534	1·5557	1·5596
μ KCl	1·4837	1·4882	1·4927	1·4976	1·4981	1·5003	1·5019

and for the ultra-violet rays:

Wave-length	8307	5540	3320	2076	1511	978	831
μ NaCl	1·5138	1·5184	1·5230	1·5264	1·5280	1·5321	1·5347
μ KCl	1·4683	1·4700	1·4720	1·4747	1·4764	1·4798	1·4822

According to N. Lagerborg, the refractive index of sodium chloride for sodium light decreases with a rise of temp. such that this constant at a temp., θ, has the value $1·54489-0·0000307\theta$ between 14·5° and 42·5°; and $1·54489-0·0000343\theta$, between 14·5° and 90·5°; and, according to T. Liebisch, for sodium chloride, $1·49110-0·0000345\theta$. Blue rock-salt shows spectral absorption bands in the red and orange, and the middle of the band corresponds with a wave-length $\lambda=630\mu\mu$; and with the blue crystals coloured by sodium [54] there is a strip in the yellow for $\lambda=562\mu\mu$. The refractive index of crystals of rubidium chloride for the *D*-line is 1·4928. The **dispersive power** of rock-salt $(\mu_C-\mu_F)/\mu_D-1)$ for the red hydrogen *C*-line (6563), the yellow sodium *D*-line, and greenish-blue hydrogen *F*-line, is 0·0233; and for sylvine, 0·0226. Rock-salt has $\mu_C=1·5407$; μ_F, 1·5534; and μ_{Na}, 1·5443; and sylvine has $\mu_C=1·4872$; μ_F, 1·4983; μ_{Na}, 1·4904. H. H. Marvin has also studied the optical dispersion. A rose-red fluorescence has been observed with violet and blue rock-salt, but not with brown, yellow, or orange-coloured salt. W. C. Röntgen also showed that rock-salt becomes luminous under the *X*-rays, and S. Kreutz has shown that some varieties of naturally coloured rock-salt, on warming, become feebly but clearly phosphorescent. V. Meyer measured the **magnetic rotatory dispersive power** of rock-salt and sylvine.

Some of G. P. Baxter's values [55] for the **refractive indices of aqueous solutions** of lithium, sodium, and potassium chlorides, at 25°, are given in Table XX. The percentage composition and sp. gr. of the soln. are also indicated in the table. O. Pulvermacher has measured values for soln. of sodium chloride. F. L. Haigh gives for normal soln. of the alkali chlorides:

	LiCl	NaCl	KCl	RbCl	CsCl
Index of refraction	1·33648	1·33751	1·33743	1·33785	1·33902

The specific and mol. refractions were also computed by Lorentz and Lorenz's formula. The increments in the densities and indices of refraction were found to decrease slowly with increasing conc., and to be nearly additive at eq. conc.—particularly with the more dil. soln. The specific refractions calculated on the assumption that the specific refraction of water does not change in soln. are nearly constant, but decrease slightly with increasing conc. The curves showing the relation between conc. and the indices of refraction of these soln. are slightly convex towards the conc. axis, corresponding with a slow decrease in the increments of the refractive index with increasing conc. The electrical conductivity [56] of crystals of sodium chloride are greatest perpendicular to the cubic faces, and least, perpendicular to the rhombic dodecahedral face.

TABLE XX.—REFRACTIVE INDICES OF SOLUTIONS OF THE ALKALI CHLORIDES.

Lithium Chloride.			*Sodium Chloride.*			*Potassium Chloride.*		
Per cent.	Density.	μ	Per cent.	Density.	μ	Per cent.	Density.	μ
0·6254	1·00068	1·33388	0·5280	1·00079	1·33342	0·9466	1·00308	1·33376
1·4114	1·00511	1·33555	0·9980	1·00413	1·33417	2·4623	1·0124	1·33581
2·7703	1·01311	1·33842	1·1068	1·00477	1·33438	4·8340	1·0282	1·33896
5·7352	1·02966	1·34465	5·3562	1·03488	1·34169	9·4153	1·0577	1·34517
10·5860	1·05832	1·35494	5·4131	1·03532	1·34179	17·898	1·1160	1·35687
13·1099	1·07299	1·36024	14·3440	1·10146	1·35747	21·770	1·1441	1·36236

W. N. Hartley [57] found the alkali chlorides in the oxyhydrogen blowpipe flame give lines of elements with a more or less continuous **spectrum** believed to be due to the respective metals. Lithium chloride, however, gives no continuous spectrum. G. P. Thomson studied the **anode rays** from lithium chloride and other alkali halides.

The **electrical conductivity** of sodium chloride [58] is very small, less than 0·0001 units—8660×10^{-8} (mercury unit) at 20°. The electrical conductivity of the molten salt at 960° is 0·9206; and, according to L. Poincaré, at 750° the electrical conductivity is 3·339 reciprocal ohms per cubic centimetre; for potassium chloride at 75°, the conductivity is 1·908 reciprocal ohms. W. Ostwald found that in the electrolysis of molten sodium chloride with carbon electrodes, there is scarcely any formation of chlorine or sodium unless special conditions are established, but the negative electrode increases in bulk and is destroyed owing to the cataphoresis of the molten chloride. The positive electrode is not affected. The electrolysis of molten sodium chloride furnishing sodium and chlorine, and of sodium chloride soln. furnishing sodium hydroxide, chlorine, and oxy-chlorine compounds are discussed in connection with the latter. E. Briner and co-workers have compared the current yields of alkali hydroxides by the electrolysis of soln. of lithium, sodium, and potassium chlorides of different conc. With 50,000 coulombs through 3·1*N*-soln. the current yields are respectively 75, 82·5, and 87 per cent. J. C. Ghosh measured the conductivity of fused sodium or potassium chloride; C. Sandonnini, mixtures of the two chlorides; and F. M. Jäger and B. Kampe found the mol. conductivity of potassium chloride, μ, at θ° between 775·7° and 943·5° to be $\mu=115{\cdot}4+0{\cdot}2575(\theta-800)$.

The **equivalent electrical conductivities of solutions** of the alkali chlorides [59] containing a mol. of the salt in *v* litres of water, at 25°, are:

v	32	64	128	256	512	1024
LiCl	103·8	106·5	109·8	112·4	114·6	116·1
NaCl	107·2	110·3	112·6	114·7	116·6	117·8
KCl	127·4	130·3	133·1	134·9	137·6	138·8
RbCl	129·6	134·0	136·9	138·6	140·0	142·0
CsCl	129·9	133·9	136·8	138·6	140·8	143.0

O. Gropp measured the conductivity of liquid and frozen soln. of lithium, sodium, and potassium chlorides. F. Ratig studied the electro-chemical action—*vide* **alkali chlorates.** The electrical conductivity of soln. of lithium chloride in several non-aqueous solvents has been investigated. Formic acid as a solvent exerts an ionizing power of the same order of magnitude as water; in acetic acid, the lithium chloride seems to be partially associated to double molecules, Li_2Cl_2; and in some solvent, the results are still further complicated by the union of the salt with the solvent. According to H. E. Patten and W. R. Mott, the electrolysis of soln. of lithium chloride in some of the higher alcohols—*e.g.* phenol—furnishes metallic lithium when the rate of the reaction between the solvent and the deposited metal is not greater than the rate of deposition of the metal. S. von Lasczynsky and S. von Gorsky measured the conductivity of lithium chloride in pyridine; B. Schapire of sodium and potassium chlorides in aq. alcohol. H. Zanninowich-Tessarin measured the electrical conductivity of soln. of potassium chloride in formic acid; and J. C. Ghosh in mixtures of pyridine and water.

The electrical conductivities of soln. of potassium chloride have been determined with a great degree of precision since aq. soln. of this salt are commonly used as normal standard liquids for measuring the resistance-constants of the apparatus employed in conductivity determinations. According to C. Déguisne, the coeff. K at $\theta°$ in reciprocal ohms is represented by the expression $k_1[1+a(\theta-18)+b(\theta-18)^2]$, where k_1 is the conductivity at 18°, and for 0·0001*N*-soln. of potassium chloride a=0·02194, b=0·0000824; for 0·001*N*-soln., a=0·02172, b=0·0000667; for 0·01*N*-soln., a=0·02149, b=0·0000653; and for 0·05*N*-soln., a=0·02127, and b=0·0000613. The limiting value of the eq. conductivity at 18° determined by F. Kohlrausch, A. A. Noyes and W. D. Coolidge, A. J. Weiland, S. J. Bates, C. A. Kraus and W. C. Bray, R. Wegscheider, W. Sutherland, H. C. Jones, P. T. Muller and R. Romann, and P. Walden varies from λ_∞=127·5 to 131·4.

The measurements of the lowering of the vap. press., the raising of the b.p., the depression of the f.p., and the electrical conductivities of aq. soln. of the alkali chlorides are in harmony with the assumption that there is a partial ionization of the salts in soln. The **degree of ionization** of soln. of potassium, sodium, and cæsium chlorides of conc. *N*-mols. per litre is:

N.	0·0001	0·001	0·01	0·1	1·0	3·0	5·0
LiCl	—	98·0	92·0	84·0	—	—	—
NaCl	99·2	97·7	93·5	84·4	68·2	—	39·2
KCl	100·0	99·0	96·0	96·0	75·5	67·9	—
CsCl	99·0	97·8	93·7	85·7	—	—	—

According to A. A. Noyes (1907), the degree of ionization decreases with a rise of temp. G. N. Lewis and G. A. Linhart have compared the degrees of ionization calculated by thermochemical data and by the ratio λ/λ_∞. S. Arrhenius gives for the **heat of ionization** at 35°, with $\frac{1}{10}$*N*-soln., LiCl, −399 cals.; NaCl, −454 cals.; and KCl, −362 cals.

The **transport number** of the lithium ion [60] at the limit of dilution at 18° is 0·330; for 0·2 to 0·0006 normal soln. of potassium chloride, the transport number of the cation is 0·494 between 0° and 18°; at 30° the constant rises to 0·499 for the anion, in soln. between 0·3 and 0·008 normality, at 18°, the transport number is 0·503, and this constant rises to 0·513 at 76°. The transport number of the anion in 0·05*N*-soln. of rubidium chloride at 20°–22° is 0·515; and in cæsium chloride soln., 0·508. With soln. of sodium chloride, the transport number of the anions at 10° rises from 0·621 with 0·005*N*-soln. to 0·648 with 3*N* to 5*N*-soln.; and for the cation in one per cent. soln., at 20°, the transport number is 0·608, and at 95°, 0·551. S. A. Braley and J. L. Hall measured the transport numbers of potassium and sodium in mixed soln. of their chlorides. G. von Hevesy estimated that the velocity of diffusion of ions in crystals of rock-salt is 3×10^{-18} cm. per day at

ordinary temp., and 200 times faster at 150°. In aq. soln. of alcohol, the transport number of the cation rises as the conc. of the alcohol increases.

The effect of press. on the electrical conductivity, resistance, degree of ionization of potassium and sodium chlorides has been measured by I. Fanjung,[61] S. Arrhenius, F. Körber, S. Lussana, G. Tammann, J. Fink, and A. L. Stern. The results of F. Körber for the ratio of the electrical resistance R_p at a press. p and R_1 at unit press. with N-soln. of the alkali halides, and with soln. of sodium chloride of different conc., are indicated in Figs. 25 and 26. F. W. Schmidt has investigated the influence of press. on soln. of the alkali halides in different solvents, and at different temp., and different conc. H. S. Harned measured the **electromotive force of cells** H_2/KCl (or NaCl), HgCl/Hg; J. A. Beattie and D. A. McInnes made observations on this subject. D. A. Innes and K. Parker, and M. Chow calculated the **free energy** of potassium chloride in soln. A. Reis gave for the free energy for the separation of ions, KCl, 163 kgrm. cals. per mol.: NaCl, 182; LiCl, 179; and HCl, 326. P. D. Foote and F. L. Mohler found the **ionizing potential** of sodium and potassium chloride vapour to be about 5 volts.

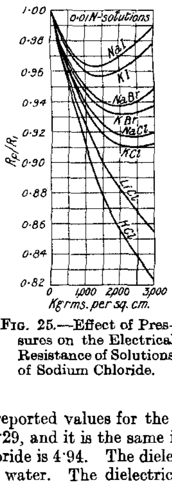

FIG. 25.—Effect of Pressures on the Electrical Resistance of Solutions of Sodium Chloride.

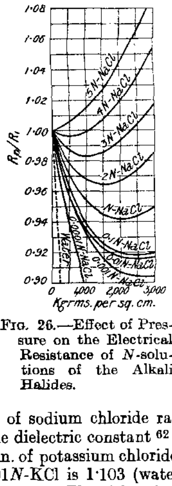

FIG. 26.—Effect of Pressure on the Electrical Resistance of N-solutions of the Alkali Halides.

The reported values for the **dielectric constant** of sodium chloride range from 5·60 to 6·29, and it is the same in all directions; the dielectric constant [62] of potassium chloride is 4·94. The dielectric constant of soln. of potassium chloride is larger than for water. The dielectric constant of a 0·001N-KCl is 1·103 (water-unity); 0·005N-KCl, 1·034; 0·01N-KCl, 1·113; 0·03N-KCl, 1·160. The dielectric constants are not proportional to the electrical conductivities. Sodium chloride is paramagnetic,[63] and the **magnetic susceptibility** of sodium chloride is $-3·76^{-7}\times10^{-7}$ units of mass, and $-8·16\times10^{-7}$ units of volume; of potassium chloride $-4·7\times10^{-7}$ mass units; of cæsium chloride, $-2·8\times10^{-7}$ mass units at 17°; and of lithium chloride, $-4·7\times10^{-7}$ mass units.

Chemical properties.—Sodium chloride is necessary for the proper performance of the physiological functions of the body; the other alkali chlorides are said to be poisonous [64] with small animals. According to C. Richet, the maximum dose per kilogram of animal, with subcutaneous injections, is 0·1 grm. with lithium chloride; 0·5 grm. with potassium chloride; 1·0 grm. with rubidium chloride; and 0·5 grm. with cæsium chloride. Lithium chloride is very hygroscopic; sodium chloride is less hygroscopic, but it takes up 0·5 to 0·6 per cent. moisture on exposure

to air. There is virtually no *hydrolysis in aqueous solutions* of sodium chloride, but at higher temp. the salt is decomposed as discussed in connection with the formation of sodium hydroxide. This is shown by F. Emich's experiment [65]:

Heat a little sodium chloride in a platinum crucible to bright redness, and add a couple of drops of water to the hot crucible so that the water assumes the spheroidal state. In a moment, transfer the water to a beaker containing a faintly coloured soln. of blue litmus—the litmus is reddened, showing the presence of an acid—hydrochloric acid. The salt remaining in the crucible is dissolved in water, and it turns red litmus blue, showing the presence of an alkali—sodium hydroxide. There appears to be a reaction: $NaCl+H_2O \rightleftharpoons NaOH+HCl$, and the water abstracts the more volatile hydrogen chloride.

Lithium chloride is more hydrolyzed in aq. soln. than sodium chloride, and this requires some attention in analysis. During the evaporation of an aq. soln. of lithium chloride, some hydrogen chloride is lost, and a mixture of the hydroxide and chloride remains. To prevent the hydrolysis, the evaporation is either conducted in a stream of hydrogen chloride gas, or the soln. to be evaporated is mixed with ammonium chloride; in the latter case, the ammonium chloride splits into ammonia and hydrogen chloride, which prevents its hydrolysis. The action of steam on heated sodium chloride can be recognized at 700°, and increases regularly with rise of temp. up to 1000°. Sodium chloride has an appreciable vap. press. at its m.p., and the reaction appears to take place mainly between salt vapour and steam. Sodium and potassium chlorides are not altered in composition by fusion in air, but lithium chloride becomes alkaline and loses chlorine.[66] According to H. Schulze, if sodium chloride be heated to redness in the presence of oxygen, a trace of chlorine is produced. If heated with phosphorus, arsenic, or molybdic trioxide, an acid chloride or chlorine is produced. Many acids decompose sodium chloride with the evolution of chlorine—*e.g.* nitric and boric acids. Alumina, boric oxide, and silica similarly decompose molten sodium chloride, and, in the presence of moisture, hydrogen chloride with sodium aluminate, borate, or silicate is respectively produced. A mixture of ferrous sulphate and sodium chloride furnishes chlorine and sodium sulphate when roasted in air; [67] ammonium hydrogen sulphate gives sodium ammonium hydrosulphate and hydrogen chloride, and at a higher temp., sodium hydrogen sulphate and ammonia. The transformation of the chloride to fluoride occurs when fluorine is brought in contact with the alkali chloride in the cold; bromine forms about 5·5 per cent. of bromide at ordinary temp., and 7 per cent. at about 400°; iodine also replaces part of the chlorine from sodium chloride. Sodium and potassium chlorides copiously absorb hydrogen chloride, and, according to M. Berthelot,[68] the respective *hydrochloride* is formed. The hydrochloride is decomposed by water. When sulphur is melted with alkali chloride, the alkali sulphide and sulphur chloride are formed.[69] Hydrogen sulphide can also transform the molten chloride into sulphide, and the action is faster in the presence of moisture.[70] The vapour of anhydrous sulphuric acid is absorbed by sodium chloride forming a syrupy mass which becomes crystalline. C. Schultz-Sellack supposes that a product with the composition $NaCl.4SO_3$ is formed. The so-called **sulphalite,** $3Na_2SO_4.2NaCl$, occurs in the borax lake district (California) as a rare crystalline mineral of sp. gr. 3·5, which is sparingly soluble in water.

An aq. soln. of sodium chloride is partially decomposed by carbon dioxide under press., and some sodium carbonate is formed. Copper, zinc, iron, lead, and aluminium give basic chlorides with aq. soln. of sodium chloride. The reported evolution of hydrogen when magnesium is used is probably due to the presence of sodium as an impurity with the metal. Lead oxide in the presence of lime gives caustic soda. Metal sulphates commonly give sodium sulphate by double decomposition: $MSO_4+2NaCl=Na_2SO_4+MCl_2$.

Several **hydrates** of lithium chloride have been reported. The existence of a **monohydrated sodium chloride,** $NaCl.H_2O$, is doubtful. E. Bevan [71] claimed to

have made it by cooling a soln. of the salt in hydrochloric acid. The so-called decahydrated *sodium chloride*, $NaCl.10H_2O$, is a eutectic mixture of ice and salt, freezing at $-21·2°$. According to J. T. Lowitz,[72] a **hydrated sodium chloride,** $NaCl.2H_2O$, is formed when a sat. soln. of salt is cooled below $-5°$. The monoclinic crystals are isomorphous with the corresponding bromide, $NaBr.2H_2O$. Hydrates of the other alkali chlorides have not been prepared.

Aq. soln. of lithium chloride absorb larger amounts of ammonia than water alone, owing to the formation of complexes, $LiCl(NH_3)_n$—**lithium ammino-chlorides.** *Similar remarks apply to lithium bromide and iodide. If the solubility of ammonia* in water be unity, R. Abegg and H. Riesenfeld found the solubility at 25° is :

	LiCl	LiBr	LiI	NaCl	NaBr	NaI	KCl	KBr	KI
0·5*N*-soln.	0·980	1·001	1·030	0·938	0·965	0·995	0·930	0·950	0·970
1·5*N*-soln.	1·045	1·900	1·190	0·843	0·890	0·985	0·809	0·857	0·900

The vap. press. *p* of ammonia in normal soln. of ammonia at 25° when *C* mol. of lithium, sodium, or potassium chlorides are dissolved in a litre of the liquid :

C	0·0	0·5	1·0	1·5
p,LiCl	13·45	13·72	13·35	12·87 mm.
p,NaCl	13·45	14·32	15·14	15·96 mm.
p,KCl	13·45	14·49	15·53	16·63 mm.

The tendency of the lithium salts to form complexes with ammonia is likewise shown by the partition of ammonia between chloroform and aq. soln. of the lithium salt.[73] Dry salts of lithium also form complexes with ammonia, and a comparison of the observed thermal value of the reaction with that computed from the dissociation press. of Clapeyron's equation has been made by J. Bonnefoi, and indicated in Table XXI. According to F. Ephraim, lithium tetrammino-chloride has a vap. press. of 760 mm. at 12°.

TABLE XXI.—DISSOCIATION PRESSURES OF THE LITHIUM AMMINO-CHLORIDES.

Formula.	Temp. of formation.	Dissociation press. mm. mercury.	Thermal value in Cals.	
			Calculated.	Found.
$LiCl.NH_3$	Over 85°	367 at 96° ; 646 at 109·2°	11·93	11·87
$LiCl.2NH_3$	60° to 85°	373 at 68·8° ; 980 at 89·2°	11·62	11·49
$LiCl.3NH_3$	15° to 60°	320 at 43° ; 790 at 60°	11·07	11·10
$LiCl.4NH_3$	−18°	384 at 0° ; 754 at 12·74°	8·93	8·93

The lithium chloride obtained by withdrawing ammonia from the ammino-chloride is in rather a favourable condition for the reformation of these compounds, and it is used for preparing analogous compounds with the mono-, di-, or tri-, methyl-, ethyl-, isobutyl-, or amylamine. According to T. Weyl,[74] potassium and sodium chlorides absorb water-free ammonia at high press. There appears to be no chemical combination, and the mass rapidly loses the absorbed gas on exposure to the air. Sodium chloride dissolves in liquid ammonia at $-10°$, and if the soln. be evaporated below $-24°$, small, white, needle-like crystals are formed with a composition corresponding with **sodium pentammino-chloride,** $NaCl.5NH_3$, and a vap. press. of 777 mm. at $-24°$, and 2130 mm. at $-7°$. A mixture of the soln. of sodium and sodium chloride in liquid ammonia becomes colourless, and gives off hydrogen with the formation of what A. Joannis[75] supposed to be $NaCl.NaNH_2$.

It has been shown that the f.p. curves of binary mixtures of the alkali chlorides show the probable formation of compounds, LiCl.RbCl, LiCl.CsCl, and LiCl.2CsCl. The curves of binary mixtures of lithium chloride with magnesium, calcium, strontium, or barium chloride show no signs of the formation of definite compounds,

but mixtures of potassium and calcium chlorides shew a maximum at 740°, corresponding with the formation of a compound, $KCl.CaCl_2$, or $KCaCl_3$. R. Krickmeyer also could not obtain solid soln. of lithium chloride with potassium or sodium chloride by crystallization from aq. soln. Lithium chloride readily forms double salts with copper, ferrous, cobalt, nickel, and uranium chlorides.[76] Potassium chloride forms a double compound, $KCl.ICl_3$, with iodine trichloride; double chlorides of cæsium or rubidium with arsenic, antimony, and bismuth chlorides; and of cæsium chloride with stannous chloride are known; and F. Rudorff[77] claimed to have made $KCl.2As_2O_3$ and $KCl.As_2O_3$ by the action of potassium chloride and arsenite.

Rubidium and cæsium chlorides readily form polyhalides with the halogens. H. L. Wells and H. L. Wheeler showed the existence of four series of chlorohalides, the one series is typified by cæsium chlorodiiodide, CsI_2Cl; and by cæsium chlorodibromide, $CsBr_2Cl$, which is formed as a dense yellow precipitate when bromine is added to a conc. soln. of cæsium chloride; another series is typified by cæsium dichlorobromide, $CsBrCl_2$; or cæsium dichloroiodide, $CsICl_2$; a third by cæsium chlorobromiodide, CsIBrCl; and a fourth by cæsium tetrachloroiodide, $CsICl_4$—the lithium and sodium analogies of the latter are alone hydrated. The iodide series is described in connection with the polyiodides, the bromide series in connection with the polybromides.

Molecular weights.—The composition of the alkali chlorides has been established by analyses. These salts contain alkali, R, and chlorine, Cl, in the proportion 1 : 1. Consequently, the mol. formulæ are represented by R_nCl_n. The difficult volatility of sodium chloride—contrasted with say mercuric chloride—suggests a complex molecule. W. Nernst[78] found the vapour density of both sodium and potassium chlorides, at 2000°, corresponded with the respective formula NaCl and KCl for the vapours of these salts. L. Rügheimer found that the effect of sodium chloride on the b.p. of bismuth trichloride corresponded with the simple formula NaCl; and E. Beckmann obtained a similar result from the effect of sodium, potassium, rubidium, and cæsium chlorides on the f.p. of mercuric chloride.

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§ 16. Ammonium Chloride

In 1705, L. Lemery [1] first showed that ammonium chloride exists among the products derived from volcanoes, where he found it admixed with sodium chloride, and this fact was verified by F. Seras in 1737, and by F. de Bonderoy in 1765. Ammonium chloride occurs as a sublimate mixed with other volatile matters in cavities

in the neighbourhood of volcanoes and in crevices in volcanic lava—*e.g.* at Etna, Vesuvius, Stromboli, Hecla, the Sandwich Islands, etc. It has been also found in the vicinity of ignited coal seams—*e.g.* at St. Etienne, Aveyron, Newcastle-on-Tyne, Bradley (Staffs), Hurlet (Renfrewshire), West Wemyss (Fife), Arniston (Midlothian), Bucharia, Kilauea (Hawaii), Waldenburg, Kattowitz, and at Duttweiler (Prussia).[2] It has been reported in guano from the Chincha Islands; in natural salt;[3] in the mother liquor of some brine springs—*e.g.* Halle—and W. Diehl found about 0·01 per cent. of ammonium chloride in carnallite from Stassfurt. It has also been found in small quantities in the secretions and exudations of animals—*e.g.* the urine of the camel.

Ammonium chloride is formed during the mixing of equal volumes of ammonia and hydrogen chloride gases. When the two gases meet a white cloud of ammonium chloride appears, but not, say H. von Helmholtz and F. Richarz,[4] if the gases be previously dried. H. B. Baker showed that combination does not occur if the gases be thoroughly dried, and that a minute quantity of water is necessary for the reaction. If the dried mixed gases be confined in a vessel fitted with platinum plates with opposite electrical charges, the two gases are separated—the ammonia collects about the negatively charged plate, and the hydrogen chloride at the other electrode. The action is not electrolytic since no discharge occurs.

Ammonium chloride is also formed by the action of hydrochloric acid on a soln. of ammonia or ammonium carbonate; J. G. Gentele[5] made it by the double decomposition of ammonium bicarbonate and sodium, magnesium, calcium, and other chlorides; H. J. E. Hennebutte and E. Mesnard, and A. Dubosc and M. Heuzey, made it by the action of ammonium bicarbonate or sulphate on the double chloride of iron and calcium; and it is made by the action of soln. of ammonium sulphate and sodium chloride; when the soln. is conc. the crystals of sodium sulphate separate out and they are removed by suitable shovels; the conc. soln. of ammonium chloride which remains is purified by crystallization. Ammonium chloride can also be obtained by sublimation from a dry intimate mixture of the same two salts. A. French made it by the joint action of air and steam on a mixture of salt, pyrites, and carbon or organic matter: $2NaCl+4H_2O+SO_2+C+N_2=2NH_4Cl+Na_2SO_4+CO_2$.

Ammonium chloride has been observed as a product of many reactions—*e.g.* the thermal decomposition of ammonium perchlorate, hydroxylamine hydrochloride, or hydrazine dihydrochloride, $N_2H_6Cl_2$; the action of hydrogen chloride on anhydrous azoimide: $3N_3H+HCl=NH_4Cl+4N_2$; the action of ammonia on chloramine: $3NH_2Cl+2NH_3=3NH_4Cl+N_2$; etc. J. Raschen and J. Brock[6] patented a process in which nitrosyl chloride, NOCl, mixed with hydrogen is passed over heated platinized asbestos: $NOCl+3H_2=NH_4Cl+H_2O$. Various proposals have been made to recover the ammonium chloride formed in the ammonia-soda process when $NaCl+(NH_4)HCO_3=NaHCO_3+NH_4Cl$.

Ammonium chloride was formerly obtained in Egypt as a product of the combustion of camels' dung, which always contains some sodium chloride; the ammonium chloride was isolated as a sublimate from the soot. In India dung was mixed with salt and similarly treated. Other nitrogenous products can be treated in a similar way. The aq. liquids which collect during the distillation of nitrogenous organic substances, which contain chlorides, also contain ammonium chloride in soln. with other ammoniacal products. For example, the ammonia liquor of gasworks, coke-oven plants, shale works, and blast furnaces is a soln. of ammonia together with a great many salts of ammonium—*e.g.* ammonium carbonate, sulphide, sulphate, cyanide, etc.—and if the coal contains sodium chloride—salty coal—the gas liquor is almost certain to contain some ammonium chloride. In any case, if the ammoniacal liquor be neutralized with hydrochloric acid, the ammonium salts are in a great measure converted into an impure ammonium chloride. M. Adler[7] converted the ammonium salts in the liquor into the chloride by treatment with calcium chloride; A. Wülfing used ferrous chloride.

It is also practicable to drive off the ammonia from the ammoniacal liquor

by treatment with milk of lime, and to pass the evolved ammonia into a vessel called a saturator containing hydrochloric acid, cooled by water. If the acid is more conc. than corresponds with a sp. gr. 1·1, it loses some hydrogen chloride when hot. The saturator is made of stoneware or some resistant material since hot hydrochloric acid attacks lead. The liquid in the saturator contains about 25 per cent. of ammonium chloride, and it is pumped into a large wooden tank lined with lead. A coil of lead pipe heated by steam is immersed in the liquid until a film of crystals forms on the surface. The liquid is then decanted to a leaden vessel, where it is allowed to crystallize; the crystals are removed, and the liquid run back to the evaporator along with some fresh soln. The soln. of ammonium chloride is not allowed to come in contact with iron, for during evaporation some ammonia is lost, and the acid liquid attacks iron. The ammonium salts can also be converted into the sulphate by treatment with sulphuric acid,[8] and subsequently the sulphate converted into chloride, as indicated above. Ammonium chloride is also made by neutralizing with ammonia the spent pickling liquor from galvanized iron works which contains a large proportion of ferrous chloride; or by treating with ammonium carbonate, or a mixture of ammonia and carbon dioxide, the soln. of calcium chloride obtained as a by-product in the ammonia-soda process. On evaporation, crystals of ammonium chloride are obtained after removing the precipitated ferric hydroxide, in the former case, and the calcium carbonate in the latter case.

The purification of ammonium chloride.—Crude sal ammoniac is usually contaminated with iron or tarry matters, and in consequence, the colour varies from yellow to red; it can be purified by heating it in thin layers on an iron plate hot enough to drive off the water and free acid, and to carbonize most of the tarry products. The grey mass is then sublimed. The sublimation is conducted in cast-iron pots lined internally with firebricks, and covered with a lid made of slightly concave plates. The salt to be sublimed is well dried, and heated. The pots hold about half a ton, and the sublimation occupies about five days. The sublimate forms a solid fibrous crust about 4 inches thick. The crust is easily detached from the lid; it is then broken up, separated from adhering dirt, and packed for the market in barrels or sacks. W. Hempel [9] proposed converting the crystalline salt into hard stone-like masses by press. between 50° and 100°.

In order to fix the iron and prevent its volatilization as chloride, F. C. Calvert recommended mixing the product before sublimation with acid calcium phosphate or ammonium phosphate, and M. Adler recommended superphosphate. Recrystallization after treatment of the soln. with animal charcoal has also been recommended. The iron is also said to be removed by treating the soln. with a little chlorine (not an excess), then with ammonia, and finally crystallizing the filtered soln. In his work on at. wt., J. S. Stas purified ammonium chloride as follows:

Ten litres of a boiling sat. soln. of sal ammoniac is treated with a litre of nitric acid of sp. gr. 1·4, and kept boiling as long as any chlorine is given off. The salt which separates from the liquid on cooling is dissolved in boiling water, and again boiled with $\frac{1}{20}$th of its volume of nitric acid so long as chlorine is evolved. The liquid is diluted with water until no ammonium chloride separates on cooling, and warmed with milk of lime. The ammonia which is evolved is washed with water, and absorbed in a vessel containing water. The aqua ammonia so produced is nearly sat. with hydrogen chloride. The ammonium chloride which separates from the liquid, after conc. and cooling is dried at 100° in a stream of ammonia gas, and sublimed at the lowest possible temp. into a glass balloon filled to the neck with dry ammonia gas. The chloride volatilizes without the least sign of carbonization. If the balloon is made of ordinary glass, the sublimate contains traces of sodium chloride, and calcium chloride, etc., derived from the glass. To eliminate these impurities, the salt is again sublimed in an atm. of ammonia gas, at as low a temp. as possible, using vessels of *verre dur*—hard glass—which resists attack by the vapour of ammonium chloride at the temp. of sublimation. Finally, in order to drive off the condensed ammonia, the sublimed salt is heated in the vessel in which the sublimate was collected, up to the temp. at which it gives off vapour.

The properties of ammonium chloride.—According to P. Groth, "the symmetry of the **crystals** of ammonium chloride is the same as that of potassium chloride.

Ammonium chloride does not belong to the isomorphous group: KCl, RbCl, and CsCl, but is isodimorphous therewith." Ammonium chloride crystallizes in cubes, octahedrons, and trapezohedrons belonging to the cubic system. Aq. soln. give *minute trapezoidal crystals which collect together, forming feathery masses; but* well-defined cubes are obtained from soln. containing a small quantity of manganous chloride (F. Raschig),[10] chromic chloride (J. W. Retgers), ferric chloride (R. Krickmeyer), and chromous, cadmium, nickelous, cobaltous, or ferrous chlorides; *ammonium sulphate or molybdate*; or *urea* (J. W. Retgers); octahedral crystals with aluminium chloride (J. W. Regters), etc. According to J. W. Retgers, some of the chloride is also adsorbed by the ammonium chloride. M. le Blanc and P. Rohland obtained crystalline plates from soln. containing a little ammonium *carbonate. If the vapour be condensed on a hot glass plate it forms small cubic* crystals, and this is the form in which natural sal ammoniac occurs. The ordinary sublimed salt has been partially fused, and appears as a translucent mass of fibrous crystals, very difficult to pulverize. The pulverulent form is best obtained by the evaporation of a soln. to dryness with constant stirring. According to J. S. Stas, and B. Gossner, a second modification is formed when the vapour is rapidly cooled in vacuo. **X-radiograms** of ammonium chloride by G. Bartlett and I. Langmuir show that the form stable at 20° has a central cubic lattice with a distance $3{\cdot}859\times10^{-10}$ cm. between like ions and $3{\cdot}342\times10^{-10}$ cm. between unlike ions; while the form stable at 250° has a simple cubic lattice with $4{\cdot}620\times10^{-10}$ cm. between like ions, and $3{\cdot}266\times10^{-10}$ cm. between unlike ions.

The formation of mixed crystals of ammonium and potassium chlorides was noted by *M. E. Chevreul,*[11] *A. Knop, H. Rassow, and R. Krickmeyer. According* to A. Fock, however, there is but a limited miscibility at 25° with a lacuna approximately between 18 and 97 mols. per cent. of ammonium chloride; and he found that the solubility of the mixed crystals in water at 25° indicates the formation of two solid phases, one below 18 and the other above 97 mols. per cent. of ammonium chloride; between these two limits the two phases are present in the solid state, and the sat. soln. has a constant composition. This is shown by the horizontal portion of the curve, Fig. 28. The regions where mixed crystals are formed are represented by the steep portions of the curve. By comparing this diagram with that for cæsium and mercuric chlorides, it will be observed there is no sign of the formation of a double salt of the two chlorides at 25°; nor could R. Krickmeyer detect any signs of mixed crystals of sodium and ammonium chlorides, although B. Gossner obtained a very limited miscibility with mixtures of ammonium chloride and iodide. Ammonium chloride behaves to other chlorides very like the alkali chlorides; as a rule, the nearer two chlorides are in general properties, the simpler is the binary system formed between them.

According to R. C. Wallace,[12] there is a marked change in the heat effect of ammonium chloride at 159°, and under the microscope, there is a change in the crystals at this temp. although they still remain optically isotropic, and on cooling the crystals show an appreciable contraction at this temp. R. C. Wallace believes that the more highly polymerized α-form, stable at ordinary temp., is not isomorphous with the potassium halides and ammonium iodide, but the less polymerized β-form, stable at the higher temp., is isomorphous with this series. F. E. C. Scheffer found the cooling curve with ammonium chloride to show that the transformation lags and appears considerably below the true transition temp., but in the presence of mannitol or glycerol, which act as catalysts, better results are obtained, and he finds that Wallace's result is too low, for the transition temp. is 184·5°; he obtained a similar result from his measurements of the solubility of the salt in water. The solubility curves of the two forms intersect at this temp. K. Hachmeister gave 174° for the transition temp.; and P. W. Bridgman gave 184·3°, and found that the effect of press. on this constant is as indicated in Fig. 27 and Table XXII.

TABLE XXII.—THE TRANSITION TEMPERATURE OF AMMONIUM CHLORIDE.

Press.	Transition temp.	Change of vol. c.c. per gram.	Latent heat kgrm. cals. per grm.
1	184·3°	0·0985	6·98
100	190·0°	0·1087	7·74
200	197·8°	0·1160	7·73
300	205·0°	0·1212	7·88

The published numbers[13] for the **specific gravity** of ammonium chloride range from 1·45 to 1·55; the best values range from 1·531 to 1·533 at about 4°, and 1·5256 (20°/4°) may be taken as the best representative value for the sp. gr., and 35·1 for the mol. vol. According to K. Kraut, ammonium chloride lost 48·9 per cent. by volatilization when heated eleven to twelve days on the water-bath. It volatilizes rapidly without fusion at a red heat. According to J. S. Stas, ammonium chloride forms a colourless transparent glassy crust when sublimed in a stream of ammonia, but, when sublimed in vacuo, at as low a temp. as possible, it forms a less compact translucent mass, which refracts light strongly, and has a different sp. gr. from the glassy variety. W. Biltz has studied the mol. vol.

A. Bineau (1838)[14] found that the vapour of ammonium chloride has but half

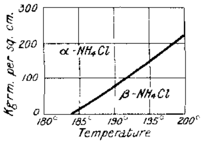

FIG. 27.—Effect of Pressure on the Transition Temperature of Ammonium Chloride.

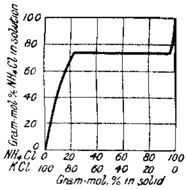

FIG. 28.—Solubility Curve of Binary Mixtures of Ammonium and Potassium Chlorides.

the density which is required on the assumption that the vapour consists of molecules of ammonium chloride, NH_4Cl; it is 29·04 at 350°, and 28·75 at 1040°—the theoretical value for the molecule is 53·5. In 1846, A. Bineau also showed that the vapour density of sulphuric acid, H_2SO_4, at 498° is likewise incompatible with Avogadro's hypothesis if the molecules of the gas have the composition H_2SO_4. He further showed that if the molecules be supposed to be broken down on heating: $NH_4Cl = NH_3 + HCl$, and $H_2SO_4 = H_2O + SO_3$, the theoretical and observed vapour densities are nearly concordant. If the vapour of ammonium chloride be completely dissociated so that a mixture of equal volumes of ammonia and hydrogen chloride is formed, the vapour density will be 26·75, that is, half the value for NH_4Cl—*i.e.* $\frac{1}{2}$ of (36·5+17). Hence it is probable that the dissociation of the vapour of ammonium chloride is nearly complete, otherwise, the at. wt. of the elements involved must be altered—thus, with NH_4Cl, instead of taking 35·5 for the at. wt. of chlorine, half this value must be employed, and instead of taking 14 for the at. wt. of nitrogen $\frac{1}{6}$ of 14, or 2·33, must be used. In the early days, these alternatives had to be considered before Avogadro's hypothesis could be admitted; accordingly, evidence for and against the alternatives was accumulated, and new examples were discovered of similar phenomena which were styled **abnormal vapour densities.** On the other hand, it did not seem likely *a priori* that molecules of steam and sulphur trioxide,

or of ammonia and hydrogen chloride, could remain in contact without chemical union, for these substances unite with vigour at ordinary temp.; but, as a matter of fact, at about 400°, there is no appreciable evolution of heat, and no other signs of chemical action when the two gases are mixed.

The main evidence for or against the alternatives must of necessity be mainly physical, because any attempt to prove dissociation or otherwise which is based upon chemical operations is confronted with the objection that the compound under investigation is thereby decomposed by the chemical agents. L. von Pebal (1862), K. von Than (1864), and others have devised experiments in which advantage is taken of the different rates of diffusion of the products of dissociation *in order to separate them partially and prevent re-combination on cooling.*

The following is typical of the more recent modifications [15] of L. von Pebal's and K. von Than's experiments to illustrate the dissociation of ammonium chloride under ordinary conditions by taking advantage of the difference in the speeds of diffusion of the two gases, ammonia and hydrogen chloride—atmolysis. Place a little ammonium chloride near the middle inside a piece of hard glass tube supported at an angle of about 30°, and a little lower down the tube place a piece of blue litmus paper. Place a loose plug of asbestos a little above the salt, and then a piece of red litmus paper. Heat the ammonium chloride. The ammonia, being a lighter gas, diffuses more quickly than the hydrogen chloride. Consequently, when the ammonium chloride is heated the blue litmus will be reddened by the excess of slow diffusing hydrogen chloride in the lower part of the tube; and the red litmus will be blued by the ammonia which passes to the upper part of the tube before the hydrogen chloride.

H. St. C. Deville (1863) found that when the two gases are mixed at 350°, the temp. rises to 395°, showing that probably some combination occurs. J. A. Wanklyn (1865) estimated from the observed vapour density, 29·04 at 350°, that about 17 per cent. of the gases unite to form ammonium chloride. J. C. G. de Marignac (1868) noticed that the heat absorbed in the sublimation of ammonium chloride is much greater than that usually observed with other substances, and is almost eq. to the heat of decomposition of the salt in question, and hence concludes: "It is very probable that sal ammoniac—in great part at least—is decomposed on volatilization."

The **vapour pressure** of ammonium chloride [16] has been determined by A. Horstmann, W. Ramsay and S. Young, etc. The following results by A. Smith and A. W. C. Menzies approximate nearest to the mean of the other values:

Temp.	280°	290°	300°	310°	320°	330°	333·5°
Vap. press.	138	189	252	336	447	587	642 mm.

Similar remarks apply to the dissociation press. calculated from the measurements of A. Smith and R. P. Calvert:

Temp.	250°	280°	310°	330°	337·8°	345°	350°
Diss. press.	49·5	135·0	341·3	610·6	760·0	927·6	1063·0 mm.

and the formula $\log p = -1920{\cdot}357/T + 9{\cdot}778609 \log T - 21{\cdot}21708$ gives results in close accord with the observed values of ammonium chloride. For tetramethyl ammonium chloride [17] at 190°, the dissociation press. is 120 mm.; at 220°, 399 mm.; at 233·3°, 760 mm., and generally, $\log p = 23649{\cdot}7/T + 132{\cdot}316 \log T - 401{\cdot}3121$.

A. Smith and R. H. Lombard have pointed out that most of the methods of determining vapour densities—*e.g.* V. Meyer's method, J. B. A. Dumas' method—are useful in detecting qualitatively the existence of dissociation, but do not show the extent of dissociation when the vapours are sat. since the vapour densities of the unsaturated vapours are alone measured, and the system therefore behaves as *if under reduced press.*, *a condition which favours dissociation.* A. Smith and R. H. Lombard's measurements of the vapour densities of sat. ammonium chloride, enable the extent of the dissociation to be calculated at different temp. Let D_0

represent the vapour density of this salt in mols. per litre if the vapour were undissociated, consequently $D_0=273P/33{\cdot}4\times760T$; also let D denote the observed vapour density ; then the degree of dissociation α in the process $NH_4Cl_{gas}\rightleftharpoons NH_3+HCl$ is $\alpha=(D_0-D)/D$. The results are :

TABLE XXIII.

Temp.	Vapour density observed. Grms. per c.c.	Mols. per litre.	Press. mm.	Percentage dissociation.
290°	169	316	185·3	67·1
300°	230	430	252·5	64·2
310°	307	573	341·3	63·8
320°	406	759	458·1	63·3
330°	531	993	808·2	63·6

The degree of dissociation with rise of temp. appears to be anomalous; but the decrease is due to the fact that the press. is not constant but rapidly increases as the temp. rises. If the press. were constant at 185·3 mm., the degree of dissociation would increase from 66 to 82 per cent. In the usual calculations of heats of dissociation, and latent heats of vaporization, it is usually assumed that the dissociation of ammonium chloride is complete, whereas actually the dissociation is between 67 and 63 per cent. between 280° and 330°.

According to H. B. Baker [18] (1894), if the vapour density of ammonium chloride be determined in a vessel of hard glass with a thoroughly dried sample of ammonium chloride, the number is quite normal, namely, 53·4. This shows that the dry salt does not dissociate quickly enough to affect the determination. A. Ladenburg (1900) refers to a statement by M. Faraday that thoroughly dried calcium carbonate is not decomposed even at high temp. under conditions where in the presence of moisture decomposition begins at once. The statement has been questioned. *Obviously, the moisture acts as a catalytic agent which accelerates not only the* dissociation, but also the formation of ammonium chloride from ammonia and hydrogen chloride. This puzzling phenomenon seems to be in direct contradiction with the theory of mass action if the dried and undried forms respectively give undissociated and dissociated vapour in equilibrium with the solid at the same temp. and press. R. Abegg (1908) drew attention to the curious feature of this reaction in that the partial press. of the undissociated ammonium chloride in equilibrium with the dried solid is practically the total press. ; while in presence of the catalyst, the equilibrium is so displaced that the partial press. of the undissociated salt is very small ; and he suggested that the heat of formation of gaseous undissociated ammonium chloride, NH_4Cl, might be just equal to the heat of dissociation of gaseous NH_4Cl into NH_3+HCl. R. Wegscheider (1909) thinks that the solid is in different polymorphic states in the two cases, and that the α-form is changed into the β-form under the influence of water vapour, while the transformation is suspended in the dried sample ; and that the high vap. press. of the ammonium chloride molecules from the undried α-form, is identical with the vap. press. of NH_3+HCl molecules from the dried form stable at 360°. It is also possible that one form has a greater internal press. than the other, and that this is brought about by the alteration of the surface conditions of one of the forms under the influence of water vapour. A similar phenomenon is shown by dried and undried calomel, and A. Smith (1910) has pointed out that both R. Abegg's and R. Wegscheider's "explanations depend upon coincidences which could not occur in precisely the same way with different substances unless the coincidences are due *to some as yet unrecognized general relation, and not to accident.*"

In accord with R. Wegscheider's suggestion, the anomaly with the α- and β-forms

of ammonium chloride may be due to ordinary α-NH_4Cl being a labile form which changes to α′-NH_4Cl at a higher temp. in the presence of moisture, and it is the transition α′- to β-NH_4Cl which occurs at 184·5°, while dry α-NH_4Cl does not change; but the assumptions that the transformation at 184·5° only occurs in the presence of moisture are untenable, because the work of F. E. C. Scheffer, and of A. Smith and co-workers, shows that the transformation occurs at this temp. with both the dry and undried salts; nor is there any evidence of any other transformation. R. Wegscheider also postulated that possibly α-NH_4Cl is stable and is transformed at 184·5° into β-NH_4Cl, but that sometimes a labile α′-form is produced in the preparation of the salt, and it is this form which evaporates without dissociation. There is yet no evidence of the existence of the assumed α′-NH_4Cl.

According to H. Fizeau,[19] the **linear coefficient of thermal expansion** of the crystals is 0·000062546 at 40°. H. Kopp gives 0·373 for the **specific heat** of the solid between 15° and 45°; and F. Neumann, 0·391, between 23° and 100°. The sp. ht. of soln. of this salt determined by J. C. G. de Marignac between 20° and 52°. for solu. of two mols. of the salt in 50, 100, and 200 mols. of water, are respectively 0·8850, 0·9382, and 0·9670. G. T. Gerlach [20] showed that if 10 and 20 per cent. soln. have unit volume at 0°, their volumes are respectively 1·0058 and 1·0072 at 25°; 1·0153 and 1·0163 at 50°; 1·0279 and 1·029 at 75°; and 1·04205 and 1·04240 at 100°.

The **latent heat of vaporization** of ammonium chloride has been determined experimentally by J. C. G. de Marignac [21] at atm. press. at 33·0 and 43·8 Cals. per mol.; this constant has also been calculated from vap. press. data by A. Horstmann and F. M. G. Johnson using Clausius and Clapeyron's equation $l=Tdp/dT(v_1-v_2)$. In no case is the evidence that the vapour had assumed the equilibrium conditions satisfactory, and A. Smith and R. H. Lombard also apply Clausius and Clapeyron's equation to the measurements of A. Smith and R. P. Calvert of the sat. vap. press. of ammonium chloride. The value of dp/dT was calculated from their vap. press. equation $\log p=-a/T+b\log T+c$; the volume of the solid v_2 is negligibly small, and that of the vapour is equal to the reciprocal of the mol. vapour density $1/D$. Substituting these values in Clausius and Clapeyron's equation there results:

$$\text{Latent heat of vaporization}=T\frac{P}{760}\left(\frac{a}{0\cdot4343T^2}+\frac{b}{T}\right)\frac{0\cdot02419}{D}\text{ Cals.}$$

where $a=1920$, and $b=9\cdot779$. Consequently, the latent heat of vaporization ranges from 32·5 Cals. at 280° to 33·3 Cals. at 330°—average 32·9 Cals. per mol. The latent heat of vaporization is virtually constant over the range 280° to 330°. The older values, 43·9 to 37·4 Cals. by A. Hortsmann, and 37·8 Cals. by F. M. G. Johnson, are larger because their vap. press. did not represent the sat. vapour, and corresponded with a greater dissociation than would be the case with sat. vapours. K. Kraut found an appreciable loss by volatilization occurs when ammonium chloride is heated on a water-bath. G. Bartha found the **boiling point** in vacuo to be 245°.

The **dissociation constants** K of ammonium chloride at different temp. calculated from the equation $K=\alpha^2D/(1-\alpha)$, where α denotes the degree of dissociation, and D the vapour densities per mol. give K=0·00432 (290°), 0·00644 (310°), and 0·0110 (330°). The interpolated values on the smoothed curve regarded as average values are respectively 0·00407, 0·00665, and 0·0106. The heat of dissociation calculated from J. H. van't Hoff's equation $d\log K/dT=+Q/RT^2$, and S. Arrhenius' relation $Q=A-CT^2$ cals. per mol., gives $4\cdot571(\log K_1-\log K_2)/(T_1-T_2)=-A/T_1T_2$. The constants A and C can be evaluated in the usual way by solving the simultaneous equations with observed values of K and T, or by graphic interpolation. A. Smith and R. H. Lombard thus obtain $A=-12800$, and $C=0\cdot00967$, and. accordingly, the **heat of dissociation** at $T°$ is $-12800-0\cdot00967T^2$ cals. per mol. Hence, the heat absorbed during dissociation increases as the temp. increases, and

the mol. ht. of the vapour of ammonium chloride is less than the sum of the mol. hts. of the products of dissociation. F. E. C. Scheffer gave 519·7° or 520° for the **melting point** of ammonium chloride.

According to M. Berthelot,[22] the **heat of formation** of ammonium chloride from its elements Cl+4H+N=76·7 Cals., and, according to J. Thomsen, 75·79 Cals. While the heat of formation $NH_{3gas}+HCl_{gas}=NH_4Cl_{solid}+44·46$ Cals. (A. Raabe), 41·91 Cals. (J. Thomsen). F. E. C. Scheffer estimated the heat of transformation from the α-form to the β-form to be −1030 cals., but R. Wegscheider calculated a value four times as large as this one. The **heat of neutralization**, NH_3+HCl, in aq. soln. is 12·27 Cals. according to J. Thomsen, and 13·536 Cals. according to P. A. Favre and J. T. Silbermann; according to F. Rüdorff, the soln. of 30 parts of salt in 100 parts of water lowers the temp. from 13·3° to −5·1°. The **heat of solution** is −3·88 Cals. According to J. H. Long, the soln. of a mol. of the salt in 150 mols. of solvents is attended by the absorption of −4·0 Cals. at 10°; and with 200 mols. of the salt, −3·9 Cals. If a soln. of 2 mols. of ammonium chloride in 20 mols. of water be diluted with n mols. of water, the thermal value of the reaction is $n=50$, −0·174 Cal.; $n=100$, −0·242 Cal.; $n=200$, −0·258 Cal.; $n=400$, −0·258 Cal. F. R. Pratt has studied the heats of dilution of soln. of ammonium chloride; and E. F. von Stackelberg gives for the heat of soln. Q of n mols. of ammonium chloride in 100 mols. of water, $Q=3930-33n-0·6n^2$ cals.

The **solubility** of ammonium chloride in water,[23] in grams of salt per 100 grms. of soln.:

	−15°	0°	20°	40°	60°	80°	100°	115°
Grms. NH_4Cl	19·7	22·7	27·1	31·4	35·6	35·6	43·6	46·6

The cryohydric mixture[24] contains between 22·9 (L. C. de Coppet) and 24·2 (P. A. Meerburg) grms. of salt per 100 grms. of water, and the cryohydric or eutectic temp. is between −15·8° and −16°. F. E. C. Scheffer found the solubility of the modification of ammonium sulphate, stable below 184·5° to be $-\log S=464·5/T-0·5400$; and of the form stable at higher temp. $-\log S=327·8/T-0·2412$, where S denotes the number of mols. of the salt in a mol. of the sat. soln. E. F. von Stackelberg[25] found the solubility between 18·5° and 19° to be depressed 272 mgrms. and 258 mgrms. per gram of soln. on raising the press. from 0 to 500 atm., *i.e.* about 2·8 mgrms. per 100 atm.

The solubility of ammonium chloride[26] is depressed by the addition of chloride ions either as hydrochloric acid or as sodium chloride, or as ammonium carbonate. For hydrochloric acid, R. Engel found at 0°, with water alone 24·61 grms. of ammonium chloride per 100 grms. of soln.; with 1·05 grms. HCl, 23·16 grms. NH_4Cl; with 7·74 grms. HCl, 14·54 grms. NH_4Cl; and with 22·07 grms. HCl, 4·67 grms. of NH_4Cl per 100 grms. of soln. With ammonia, the lowering of the solubility is small since only a relatively small proportion of the ammonia in soln. forms NH_4-ions, and ammino-compounds are likewise formed in the soln. R. Engel[27] found that for 100 grms. of soln.:

NH_4OH	0·92	2·05	9·30	13·66	15·36	16·29	22·18	28·97
NH_4Cl	24·52	24·35	23·35	23·09	23·56	23·75	26·63	32·14

The increase in the solubility corresponds with the formation of ammino-compounds. Some of these were prepared by L. Troost by the action of dry ammonia on dry ammonium chloride at a low temp. Thus, **ammonium triammino-chloride**, $NH_4Cl.3NH_3$, forms double refracting crystals which melt at 7°. J. Kendall and J. G. Davidson studied the f.p. curves of mixtures of ammonia and ammonium chloride, and isolated the triammino-salt, m.p. 10·7°; no evidence of an hexammino-salt was observed. The dissociation press. of $NH_4Cl.3NH_3=NH_4Cl+3NH_3$ at −36° is 140 mm.; and −20°, 310 mm.; at 6°, 730 mm.; at 0°, 1035 mm.; at 6°, 1480 mm.; and at 8·0°, 1800 mm. **Ammonium hexammino-chloride**, $NH_4Cl.6NH_3$, melts at −18°, and it is easily undercooled. The dissociation press., $NH_4Cl.6NH_3=NH_4Cl.3NH_3+3NH_3$, at −36° is 580 mm.; at −31·1°, 750 mm.; at −27°, 895 mm.;

and at −21°, 1130 mm. Ammonium chloride dissolves in liquid amn about −35° somewhat copiously, and the conductivity of dil. soln. than aq. soln., and that of conc. soln. less. This is explained by assumin mobilities are greater in liquid ammonia, while the ionizing power o greater than liquid ammonia. At a dilution v=100, the degree of dissc liquid ammonia is 0·39 (−33°); and in water, 0·85 (18°). H. Moissan electrolysis of soln. of ammonium chloride in liquid ammonia at −60° ga at the positive pole which at this temp. does not act on the ammonia; h given off at the negative pole.

F. Rüdorff[29] found that if both salts are present in the solid phase, of water dissolve 29·2 of NH_4Cl, and 174·0 of NH_4NO_3 (19·5°); 26·8N 46·5$(NH_4)_2SO_4$ (21·5°); 33·8NH_4Cl and 11·6$BaCl_2$ (20°); 28·9N 16·9KCl (15°); 30·4NH_4Cl and 19·1KCl (22°); 36·8NH_4Cl and 14·1K_2S 18·7NH_4Cl and 23·9NaCl (18·7); G. Karsten found 39·2NH_4Cl and 17·((18·5°); 38·8NH_4Cl and 34·2KNO_3 (14·8°); 39·8NH_4Cl and 38·6KNO 37·9NH_4Cl and 13·3K_2SO_4 (18·7°); and G. J. Mulder, 67·7NH_4Cl an at the b.p.

In 1854, G. Michel and F. Krafft showed that while the dissolution of is attended by a contraction, with ammonium chloride, on the contrary, t expansion. According to W. Ostwald and M. Rogow, if a mol. of a chloride of mol. wt. M, be dissolved in (2000-M) grams of water, at 20°, t increases 36·8 c.c.; J. Thomsen found an expansion of 38 c.c. by dissolv of this salt in 30–40 mols. of water; and H. Schiff and U. Monsacchi fou **specific gravities** and the expansion per 100 grms. of soln. of a chloride:

Per cent. NH_4Cl . .	5	10	15	20	25
Sp. gr. at 19° . .	1·0145	1·0293	1·0498	1·0579	1·0714
Expansion per 100 c.c. .	0·1445	1·444	0·817	1·226	1·794

According to F. L. Haigh, the sp. gr. of a N-soln. at 20°/4° is 1·01454. W. V could find no contraction during the soln. of ammonium chloride in water. . to H. Schiff and U. Monsacchi,[30] the sp. gr. D of a soln. containing p pe ammonium chloride is $D=1+0·00294p+0·0000008p^2+0·00000016p^3$, N. A. Tschernay gives for the volume v of soln. of ammonium chlori $NH_4Cl+50H_2O$, $v=1+0·0_4746\theta+0·0_53997\theta^2$; $NH_4Cl+25H_2O$, $v=1+$ $+0·0_53649\theta^2$. The **molecular volumes** of the dissolved chloride calc J. Traube from G. T. Gerlach's sp. gr. determinations are respectively : and 39·0 with 5, 20, and 25 per cent. soln. F. L. Haigh found a norm ammonium chloride expanded or contracted −31·0 c.c. per 10 litres from −19·7 from 20° to 10°; 28·0 from 20° to 30°; 62·8 from 20° to 40°; from 20° to 50°.

M. Schumann found that the **compressibility** of soln. of ammonium cl represented by the decrease in millionths of the volume per atm., is, bet and two atm., 48·7 and 40·0 respectively with 5 and 20 per cent. soln. a 44·6 and 38·3 respectively with 5 and 20 per cent. soln. at 15°. Unlike soln., the compressibility decreases with rise of temp. M. Schumann[31] compressibility at 0° to be greater than that of pure water, but W. C. and J. Schneider could not confirm this. F. Braun found the compres a sat. soln. at 1° to be 0·000038. W. C. Röntgen and J. Schneider give c bilities of 0·961 and 0·933 with soln. of a mol. of the salt respectively in 700 mols. of water—*vide* ammonium iodide.

The **viscosities** of N-, $\frac{1}{2}N$-, $\frac{1}{4}N$-, and $\frac{1}{8}N$-soln. at 25° are, according to A. respectively 0·9884, 0·9976, 0·9990, and 0·9999; and F. H. Getman fc the viscosities of soln. of ammonium chloride at 25° decrease from 0·008 per cm. with 0·4437N-soln. to a minimum 0·00878 with 2·2185N-soln. to 0·00925 for 4·437N-soln. The sp. gr. of these soln. were respectivel

1·0331, and 1·0630. The viscosity of a 1·62N-soln. falls from 0·0123 at 10° to 0·0081 at 30°, and to 0·0058 at 50°. At temp. exceeding 30°, J. W. Retgers found that the viscosity of ammonium chloride soln. is greater than that of water at the same temp. With conc. soln., says R. Cohen, the increase in the viscosity of soln. of ammonium chloride is almost proportional to the percentage variation of press. According to C. Forch,[33] the **surface tensions,** σ, of soln. of ammonium chloride with 4·864, 2·432, and 0·584 mols. of the salt per litre are respectively 0·746, 0·367, 0·088 mgrm. per mm. and σ/M, 0·153, 0·151, and 0·150. The **coefficients of diffusion** of soln. with 8, 48, and 130 grms. of the salt per litre at 20° are [34] respectively 1·32, 1·37, and 1·33 grms. per cm. per day.

The **vapour pressures** of aq. soln. of ammonium chloride have been measured at different temp. and conc. by G. Tammann.[35] For one per cent. soln., F. M. Raoult obtained a lowering of $0·0565\times7·6$; and J. Walker found a mol. of the salt in 100 mols. of water lowered the vap. press. 1·99. M. Allaurd [36] found the **boiling point** of a sat. soln. of ammonium chloride to be 115·8° at 71·8 mm., and G. T. Gerlach found that a soln. of 6·5 grms. of salt per 100 grms. of water boiled at 101°; with 50·6 grms. of salt, 109°; and with 87·1 grms. of salt at 114·8°. The **freezing point** of sat. soln. is −15·8°; [37] the mol. lowering of the f.p. of the soln. with 0·0535 grm. of salt per 100 grms. of water is 3·4°, and with 5·633 grms. of salt, 3·34°. L. C. de Coppet found the mol. lowering of the temp. of the maximum density of water to be 7·07–7·26, and this increases with the conc. The f.p. determinations show that ammonium chloride is very much ionized in aq. soln. J. H. van't Hoff's [38] factor i is for 0·14N-soln. at 14°, 1·82 by H. de Vries' plasmolytic method, and according to E. H. Loomis' cryoscopic measurements, 1·85. The mol. lowering of the f.p. reaches a minimum with increasing conc., and this increases. H. C. Jones and F. H. Getman attribute this result to the formation of hydrates. Similar remarks apply to S. M. Johnston's measurements of the raising of the b.p. of soln. of ammonium chloride. The results with ammonium chloride differ in degree but agree in kind with those with the alkali chlorides. C. Brück investigated the hydrolysis of boiling soln. of ammonium chloride.

The **refractive index** of the crystals of ammonium chloride for the B-line is [39] 1·6331; C-line, 1·6365; D-line, 1·6428; E-line, 1·6453; F-line, 1·6532; and the G-line, 1·6612. M. le Blanc and P. Rohland obtained for the D-line by J. H. Gladstone and T. P. Dale's formula a refraction eq. of 22·97 (20°); and by H. A. Lorentz and L. Lorenz's formula, 12·92 (20°); and for 6·25 per cent. soln., 22·53 by the first-named formula, 13·32 by the latter. For the dispersion constant of N-soln. at 18°, $(\nu_\beta-\nu_\alpha)/\nu_D=0·035$, where ν denotes the difference in the refractive indices of water and soln. for the H_α-, H_β-, and D-lines. F. L. Haigh found the index of refraction of an N-soln. of ammonium chloride to be 1·34311. The mol. **dispersion** of a conc. soln. for the H- and A-lines is 1·52. W. H. Perkin gives 6·096 for the **molecular magnetic rotation** of a 27·08 per cent. soln. S. Procopiu studied the birefringence and dichromatism of the smoke of ammonium chloride in an electric field. O. Reinkoher studied the reflexion spectrum of ammonium chloride for **ultra-red rays.**

Although ammonia and hydrogen chloride show no conductivity by themselves at ordinary temp., dissociating ammonium chloride was found by A. de Hemptinne to be a fairly good conductor. This is also the case with ammonium bromide. The **electrical conductivity** λ of soln. containing a mol. of ammonium chloride per v litres at 25°, rises from $\lambda=127·4$, when $v=32$, to $\lambda=138·0$, when $v=1024$. According to F. Kohlrausch [40] and O. Grotrian, the specific conductivity κ at $\theta°$ is $\kappa=0·0610(1+0·0269\theta+0·000067\theta^2)$ for 5 per cent. soln., and for 20 per cent. soln., $\kappa=0·2403(1+0·0220\theta+0·000013\theta^2)$. The **transport number** [41] of the cation, $NH_4^{\cdot}$, is 0·487–0·490 at 0°, when $v=29·4$ to 120; and at 30°, 0·494–0·496, when $v=29·5$ to 120. The ionization does not follow W. Ostwald's dilution law, but it does fit Rudolphi's modification. The computation of J. H. van't Hoff's factor from the conductivity measurements agree well with the results obtained by the

f.p. method. The electrical decomposition potential[42] of an *N*-soln. with platinum electrodes at 20° is 1·70 volts, about 0·3 volt smaller than that of potassium or sodium chloride under similar conditions. H. Kolbe found that the electrolysis of conc. soln. with platinum electrodes gave neither oxygen at the anode nor hydrogen at the cathode, but drops of nitrogen chloride were formed on the cathode. S. Lussana has studied the effect of press. on the electrical properties of ammonium chloride.

C. A. L. de Bruyn[43] found 100 grms. of absolute *methyl alcohol* dissolved 3·35 grms. of ammonium chloride, and 98 per cent. methyl alcohol, 3·52 grms. G. Carrara has measured the electrical conductivity of soln. in methyl alcohol. Similarly, C. A. L. de Bruyn 100 grms. of absolute *ethyl alcohol*, dissolve 0·62 grm. of ammonium chloride, and H. A. Bathrick found 8·3 per cent. ethyl alcohol dissolves 35·3 grms. of ammonium chloride; 54·3 per cent. alcohol, 14·0 grms.; 87·9 per cent. alcohol, 2·9 grms. A. Gerardin found 11·2 grms. of ammonium chloride dissolved in 100 grms. of 45 per cent. alcohol at 4°; 19·4 grms. at 27°; and 30·1 grms. at 56°. W. Herz and M. Knoch found that a 10 per cent. soln. of *acetone* dissolved 28·59 per cent. ammonium chloride; 40 per cent. acetone, 17·59 per cent., and 90 per cent. acetone, 0·5 grm. of ammonium chloride. Soln. with between 46·5 and 85·7 per cent. acetone separate into two layers. They also found 100 per cent. *glycerol* dissolved 12·23 per cent. of ammonium chloride; 45·36 per cent. glycerol, 23·26 per cent.; and 13·28 per cent. glycerol, 29·16 per cent. Ammonium chloride is soluble in liquid *formic acid*, and the m.p. and electrical conductivity of these soln. show that this salt is ionized between 49 and 54 per cent. when the conc. is between 2·888 and 0·362 mol. per litre. L. Kahlenberg and H. Schlundt have measured the conductivity of soln. of ammonium chloride in liquid *hydrogen cyanide*. F. L. Shinn has measured the conductivity of soln. in *ethylamine*; and, according to Z. Klemensiewicz, the dil. soln. in liquid *antimony trichloride* conduct electricity better than aq. soln. L. Kahlenberg and F. C. Krauskoff find ammonium chloride to be insoluble in *pyridine*, but it is slightly soluble if water be present. M. Stuckgold found a litre of *ethylurethane* at 60° dissolves 0·025 mol. of ammonium chloride; and 0·621 of ammonium iodide.

Ammonium chloride loses ammonia when exposed to the atm., and then reddens blue litmus, but, according to J. B. Emmett, if it be heated to the point of sublimation and then dissolved in water the soln. reacts neutral. A soln. in warm water loses ammonia and reacts acid, and R. Fittig[44] showed that on distillation, an excess of ammonia collects in the early fractions. The **hydrolysis** of ammonium chloride in aq. soln.: $NH_4Cl+H_2O \rightleftharpoons NH_4OH+HCl$ is followed by $NH_4OH \rightleftharpoons NH_3+H_2O$. According to E. G. Hill, the hydrolysis constant $K\times10^5$ in $C_{HCl}C_{NH_4OH}=KC_{NH_4Cl}$ ranges from 0·0065 for *N*-soln. to 0·00684 for $\frac{1}{25}N$-soln. A. Naumann and A. Rücker measured the ratio of the ammonia in the distillate to that in the distilled soln., and estimated the degrees of hydrolysis in 4*N*- and 2*N*-soln. at the b.p. to be respectively 1·98 and 3·0 per cent. D. Vitali obtained no free iodine when potassium iodide and iodate are heated alone, but in the presence of ammonium chloride, the free acid liberates iodine and ammonia. Similarly, with bromides and bromates, and with chlorides and chlorates. S. E. Moody found that under these conditions the hydrolysis progressed to completion, and that the chloride hydrolyzes more easily than the sulphate.

A. R. Leeds reported that a soln. of ammonium chloride forms white flecks on standing a couple of years, but it is not clear whether this was not caused by the action of the soln. on the glass. Soln. of ammonium chloride, says G. Gore, are decomposed in contact with finely divided silica. A. Bineau (1838), J. S. Stas (1865), and H. B. Baker (1894) have reported that vessels made of soft, but not hard, glass are etched by the vapour of ammonium chloride, and F W. Clarke has found that ammonium chloride exerts a marked action on silicates at about 350°; this also is exemplified by J. L. Smith's process for the determination of alkalies in silicates. The corrosive action of ammoniacal vapours on the exposed

surface of glass windows in the vicinity of stables and manure heaps has been noticed.

Ammonium chloride is decomposed by **hydrogen iodide. Chromic, ferric, cupric,** and **antimonic chlorides**[45] readily dissociate when heated, are reduced to *the -ous chloride and nitrogen is formed*: $3SbCl_5+2NH_4Cl=3SbCl_3+8HCl+N_2$; and $6FeCl_3+2NH_4Cl=6FeCl_2+8HCl+N_2$. Double salts are formed with **mercuric chloride. Stannic chloride** is not reduced after many days' heating at 400°; and **titanic chloride,** $TiCl_4$, under similar conditions forms a double salt. H. N. Stokes *found that ammonium chloride forms complex chloronitrides of phosphorus when* heated in a sealed tube with **phosphorus pentachloride. Chlorine** and the **hypochlorites** form nitrogen and nitrogen chloride (*q.v.*). **Potassium chloride,** according to L. Soubeiran,[46] decomposes ammonium chloride at a temp. below the b.p. of sulphuric acid, forming a gas which smells like chlorine; the amount of chlorine evolved is proportional to the chlorine in the ammonium chloride, the nitrogen is not oxidized. K. Hachmeister found for the f.p. and b.p. of binary mixtures of ammonium and lithium chlorides with *w* per cent. of the former:

w	100	79·39	67·23	65·0	60·00	56·18	53·38	43·42
B.p.	338°	329°	334°	335°	340°	342°	342°	350°
F.p.	—	—	320°	313°	291°	—	280°	342°

The f.p. curve has a eutectic about 260°. The b.p. and the f.p. curves cut one another.

According to H. Rose,[47] dry powdered ammonium chloride at 0° absorbs the vapour of **sulphur trioxide** without decomposition, forming a hard mass which, when heated, first develops hydrogen chloride, and forms ammonium sulphate—it has been suggested that the product may be ammonium chloropyro-sulphate, $NH_4.O.S_2O_5Cl$. With **carbon monoxide** at a red heat, C. Stammer observed no changes, but with **calcium carbide,** R. Salvadori obtained calcium chloride, nitrogen, ammonia, carbon, and a series of hydrocarbons—methane, ethylene, and acetylene.

According to F. G. Mathews,[48] ammonium chloride forms some nitric oxide, *chlorine, and nitrosyl chloride,* NOCl, *when treated with* **nitric acid. Nitrites** *are* decomposed when boiled with ammonium chloride: $KNO_2+NH_4Cl=N_2+KCl+2H_2O$; and when fused with potassium nitrate, combustion attended by a purple flame takes place. In soln. there is double decomposition: $NH_4Cl+NaNO_3=NaCl+NH_4NO_3$. According to M. Berthelot, the thermal value of the reaction between a mol. of normal **sodium phosphate,** Na_3PO_4, and half a mol of ammonium chloride is 2620 cals.; and with 1, 2, and 3 mols. of ammonium chloride, 4840, 5630, and 5960 cals. respectively.

H. Davy[49] found that when heated with the **alkali metals,** ammonium chloride vapour is decomposed, forming the alkali chloride and a mixture of two volumes of ammonia and one of hydrogen. Other metals—*e.g.* **iron, tin,** etc.—act somewhat similarly. Many **oxides** and **salts** are transformed into chlorides when calcined with ammonium chloride; the **oxides of nickel** and **cobalt** are reduced to metals. **Tin** and **antimony sulphides** *are also attacked by dry ammonium* chloride vapours by the ammonia. According to C. R. A. Wright, cupric oxide is partially reduced and partially converted into the metal: $4CuO+2NH_4Cl=CuCl_2+3Cu+4H_2O+N_2$. According to L. Santi, an aq. soln. of ammonium chloride more or less readily attacks **magnesium, zinc, cadmium, chromium, manganese,** and **tin,** and, says G. Lungi, it acts more vigorously on cast **iron** or **lead** than soln. of sodium chloride; with iron a soluble double salt, $FeCl_2.2NH_4Cl$, is formed when the mixture is warmed, and hydrogen and ammonia are formed. The reactions with soln. of ammonium chloride are to a great extent interpreted on the assumption that they are produced by the hydrochloric acid developed by the hydrolysis: $NH_4Cl+H_2O=NH_4OH+HCl$. For example, the **calcium, nickel, manganese,** or **iron monoxide** *forms the corresponding chloride and ammonia. According to* M. Berthelot and G. André,[50] half an hour's boiling of ammonium chloride with soln. of **sodium**

hydroxide or **calcium oxide** liberates all the ammonia; with magnesia, only 22·3 to 24·5 of the contained ammonia was lost after an hour's boiling. According to F. Isambert, the thermal value of the reaction is $2NH_4Cl+CaO=CaCl_2+2NH_3+H_2O-10·9$ Cals.; or $2NH_4Cl+Ca(OH)_2=CaCl_2+2NH_3+2H_2O-7·55$ Cals. At ordinary temp., ammonia is not given off from the mixed soln., but rather is calcium diammino-chloride, $CaCl_2.2NH_3$, formed with the evolution of about 14 Cals. At 180°–200°, this product gives off ammonia. Similar results are obtained with **baryta** and **strontia,** but not with **lead oxide.** In consequence, ammonia is completely driven from these soln. only after vigorous boiling, and this more readily with dil. than with conc. soln. When a mixed soln. of sodium hydroxide and ammonium chloride is allowed to stand in the cold for three days, it loses but 25 per cent. of its contained ammonia. Similarly, says H. Cantoni and G. Goguelia, the carbonates form chlorides with the evolution of ammonia and carbon dioxide; and many of the sulphides are attacked, forming chloride and ammonium sulphide: $2NH_4Cl+MnS\rightleftharpoons(NH_4)_2S+MnCl_2$. In further illustrations of the chemical reactions of aq. soln. of ammonium chloride, **manganates** are converted into permanganates, **chromates** to dichromates and to chromic anhydride; **barium peroxide** in the cold gives hydrogen peroxide, and when heated, oxygen and ammonia: $2BaO_2+4NH_4Cl=2BaCl_2+4NH_3+2H_2O+O_2$; **sodium thiosulphate** decomposes: $Na_2S_2O_3+2NH_4Cl=2NaCl+H_2O+2NH_3+SO_2+S$, and the sulphur and ammonia react in warm soln., forming ammonium sulphide; and with persulphates, chlorine, nitrogen, and hypochlorous acid are formed. The **hydroxides of magnesium, zinc, cadmium,** and **manganese** are more soluble in aq. soln. of ammonium chloride than in water, owing to the formation of double salts.[51]

Uses.—Ammonium chloride is used in pharmacy; in certain galvanic batteries; and in the preparation of ammonia and ammonium salts. It is used in the manufacture of colours; in cotton printing; in tin plating; in galvanizing; and in soldering.

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§ 17. The Alkali Bromides

The history of the bromides dates from the discovery of bromine by A. J. Balard [1] in 1824. He prepared potassium bromide by the action of bromine on potash lye, and calcined the residue remaining on evaporating the product to dryness. The bromine in sea-water may be present as alkali bromide, but more probably as magnesium bromide. It is, however, uncertain how the bromides are distributed; and similar remarks apply to the bromides present in spring and mine waters. Potassium bromide is used in chemical laboratories; medicinally in some nervous diseases; and in photography.

The preparation of the alkali bromides.—While V. Merz and W. Weith [2] found that metallic sodium reacts very slowly with bromine such that even after the two elements have been kept for 8 hrs. at 200°, the conversion of sodium into the bromide is but superficial; potassium, cæsium, and rubidium unite with bromine more quickly, forming the alkali bromide. The bromides are also formed when hydrobromic acid is neutralized with the alkali hydroxide or carbonate, and the soln. evaporated. This method, for example, has been used for preparing rubidium bromide, RbBr. C. Chaubrié and N. N. Beketoff made a soln. of cæsium bromide, CsBr, by the double decomposition of cæsium sulphate, and barium bromide. F. Klein [3] made lithium bromide by digesting calcium bromide with lithium carbonate

and evaporating the clear liquid; potassium bromide was similarly prepared by treating calcium bromide with potassium sulphate; A. Faust used potassium carbonate.

O. Henry prepared sodium and potassium bromides by boiling ferrous bromide respectively with potassium or sodium carbonate until the precipitate is brown; the clear liquid was then filtered and evaporated. J. Knobloch recommended treating a mixture of ferrous bromide with milk of lime, and then with potassium sulphate if potassium bromide is desired, or with Glauber's salt if sodium bromide is to be made. The mixture is then to be boiled, the precipitated iron oxide filtered off, and the soln. evaporated, for cubic crystals of potassium bromide. This is the principle of the method employed for manufacturing potassium bromide on a large scale:

Add 15 grms. (or 5 c.c.) of bromine to 100 c.c. of water contained in a 250 c.c. flask; and with constant shaking gradually add 8 grms. of iron filings to the contents flask. If the reaction: $Fe+Br_2=FeBr_2$ promises to become too violent, cool the flask by dipping it in cold water. *Heat the flask and its contents on a water-bath until the liquid loses its brown colour.* The flask then contains a green soln. of ferric and ferrous bromide together with an excess of iron. To the filtered soln. add sufficient potassium carbonate to precipitate all the iron: $FeBr_2+K_2CO_3=FeCO_3+2KBr$, and leave the liquid slightly alkaline. Heat the mixture on a water-bath. The precipitate, at first white, rapidly becomes brown: $4FeCO_3+O_2=2Fe_2O_3+4CO_2$. *When the precipitate has settled pour off the clear* liquid, and wash the precipitate by decantation with hot water. The clear filtered liquid is evaporated for crystals of potassium bromide.

The bromides are also prepared by dissolving bromine in alkali lye. The mixture of bromides and bromates is evaporated; and calcined to decompose the bromates. The calcined mass is dissolved in water, and the soln. acidified with hydrobromic acid, and evaporated. C. Löwig recommended evaporating the soln. of mixed bromides and bromates to a semi-fluid consistency, mixing the product with powdered wood charcoal, drying, and calcining the mixture in a crucible at a red heat. The sintered mass is then to be leached with hot water, and evaporated for crystals of the bromide. C. Löwig also decomposed the bromates in the soln. by hydrogen sulphide, boiled the liquid to drive off the dissolved gas, and after filtering off the sulphur, neutralized the liquid either with hydrobromic acid or alkali lye, and evaporated to dryness.

M. Falières prepared the salt by mixing 80 grms. of bromine with a soln. of 100 grms. of potassium carbonate in 500 grms. of water; the resulting soln. of potassium hypobromite was mixed with 30 grms. of ammonia water (sp. gr. 0·875) diluted with 80 grms. of water. The liquid was evaporated to dryness, calcined, extracted with water, and the soln. allowed to crystallize. M. Castelhaz recommended saturating aqua ammonia with bromine; the ammonium bromide which crystallizes from the soln. is free from iodides since the ammonium iodide remains in the mother liquid. When a soln. of ammonium bromide is boiled with sodium hydroxide or carbonate, until the smell of ammonia has disappeared, crystals of sodium bromide can be obtained. Similar remarks apply to potassium bromide.

The impurities of potassium bromide.—Judging from the analyses of potassium bromide by H. Adrian,[4] the older commercial varieties were very much more contaminated with impurities than modern samples. For example, H. Adrian found 10 to 15 per cent. of impurities in 10 commercial samples; to-day, the German Pharmacopœia permits 2 per cent. of potassium chloride, and about 0·1 per cent. of the carbonate. There has been reported 0·13 per cent. of KCl in English bromide, 4·52 to 5·92 per cent. in American; and in both, 0·35 to 1·29 per cent. of moisture. The bromide from Stassfurt is free from iodides. To detect *iodides*, the soln. is first treated with a little fuming nitric acid, and then shaken with chloroform, if but little iodine is present, the chloroform will not be coloured, but if the bromide be treated with an excess of ferric chloride the iodine will colour the chloroform

rose-pink. If the salt be treated with potassium permanganate, the bromide will not be decomposed but the iodide will be converted into iodate. A. Baudrimont freed potassium bromide from iodide by boiling a conc. soln. with a little bromine water. The liberated iodine volatilizes with the excess of bromine during the boiling.

The properties of the alkali bromides.—The bromides of the alkalies and ammonium all crystallize in the cubic system. J. W. Retgers[5] found that cubic **crystals** are obtained with potassium bromide in soln. containing a little urea; chromic or ferric chloride; or lead chloride. The space lattice is indicated in connection with the chlorides. H. Schwendenwein studied the **space lattice** of the crystals of the alkali bromides; W. P. Davey that of rubidium bromide. K. Fajans and K. F. Herzfeld found for the distances apart of the atoms in the space lattice of sodium, potassium, and rubidium bromides, respectively $2{\cdot}980\times10^{-8}$, $3{\cdot}295\times10^{-8}$, and $3{\cdot}440\times10^{-8}$ cm., and for the respective lattice energies, 159·7, 150·4, and 146·5 Cals. per mol. E. Newbery and H. Lupton[6] found that potassium bromide is coloured sea-green by exposure to radium emanation, and it resembles the effect produced with potassium chloride. The crystals glow with a bluish light during the exposure. E. Bandrowsky[7] reported that a few faint, transient flashes of **crystalloluminescence** occur when potassium bromide is precipitated with 96 per cent. alcohol. M. Trautz was unable to get the phenomenon with the alkali bromides. E. F. Farnau claims to have observed the phenomenon with sodium bromide by adding alcohol to sat. soln. H. B. Weiser obtained negative results on repeating E. F. Farnau's experiments, but observed crystalloluminescence with potassium bromide similar in every respect to that with sodium or potassium chloride. Alcohol was not a good precipitant, but hydrobromic acid of sp. gr. 1·337 gave good results. The crystals of lithium and sodium bromides are deliquescent in air; the other three salts are not so. F. W. Clarke's[8] value for the **specific gravity** of lithium bromide is 3·485. P. A. Favre and C. A. Valson's value for sodium bromide is 3·198 (17·3°); P. Kremers', 3·079 (17·5°); H. Schiff's, 2·952; G. Tschermak's, 3·011; E. Brunner's value for the molten salt between 800° and 1000° is $2{\cdot}2125-0{\cdot}00080(\theta-900)$. G. Quincke's value at the m.p. is 2·448, R. Krickmeyer's value for potassium bromide at 0° is 2·415; at 20°, 2·756±0·003; W. Spring's, 2·704 (18°); J. Y. Buchanan's, 2·679; T. W. Richards and E. Mueller's, 2·73 (25°); and for the molten salt between 800° and 1000°, E. Brunner gives $D=1{\cdot}991-0{\cdot}00080(\theta-900)$. G. Quincke's value at the m.p. is 2·199; C. J. B. Karsten's value at ordinary temp. is 2·672; L. Playfair and J. P. Joule's, 2·672; H. G. F. Schröder's, 2·690 (water 3·9° unity); B. Gossner's, 2·754; J. A. Craw's, 2·728; and M. Sprockhoff's, 2·751; H. Topsöe and C. Christiansen's mean value is 2·681. C. Setterberg's value for rubidium bromide is 3·358; J. A. Craw's, 3·314; E. H. Archibald's, 3·282; J. Y. Buchanan's, 3·210 (23°); and M. Sprockhoff's, 3·356. C. Setterberg's value for cæsium bromide is 4·463; M. Sprockhoff's, 4·452; T. W. Richards', 4·380; N. N. Beketoff's, 4·523; J. Y. Buchanan's, 4·508 (22·8°); and G. P. Baxter and F. N. Brink's, 4·510 (25°). G. P. Baxter and C. C. Wallace's data may be taken as embodying the best representative values of the salts in question:

Temperature.	LiBr	NaBr	KBr	RbBr	CsBr
70·19°	3·446	3·186	—	—	4·406
50·04°	3·454	3·194	2·740	3·340	4·418
25·00°	3·464	3·203	2·749	3·349	4·433
0°	3·474	3·213	2·756	3·358	4·449

The mol. vol. are indicated in Table XXIV. Potassium bromide does not form mixed crystals with the sodium salt. K. Fajans and H. Grimm studied the mol. vol. of the alkali bromides. For the effect of press. on the sp. gr. see the alkali chlorides.

According to W. Müller-Erzbach, the volume contraction which occurs in the formation of the halide salts is greatest with the chlorides and least with the iodides. This is illustrated in Table XXIV.

TABLE XXIV.—VOLUME RELATIONS OF SOME HALOID SALTS.

	A	B	C	(D−B)/A	(C−D)/C
	Sp. gr.	Mol. wt.	Calc. volume.	Found volume.	Contraction.
RbCl	2·20	120·9	81·7	55·0	0·32
RbBr	2·78	165·4	81·7	59·8	0·27
RbI	3 02	212 4	81·7	70·0	0·14
LiCl	2·00	42·5	37·4	21·2	0·43
LiBr	3·10	87·0	37·4	28·2	0·25
LiI	3·49	134·0	37·4	28·1	−0·03

The sp. gr. of the molten alkali bromides are indicated in Table XXV. The sp. gr. D of molten sodium bromide at $\theta°$ (water at 4° unity) is $D=2·306-0·0072(\theta-780)-0·0000008(\theta-270)^2$; potassium bromide, $D=2·106-0·000799(\theta-750)$; rubidium bromide, $D=2·688-0·001096(\theta-700)$; and cæsium bromide, $D=3·125-0·00134(\theta-650)$. E. Brunner found for sodium bromide, $D=2·2125-0·00080(\theta-900)$. R. Lorenz and co-workers found for potassium bromide, $D=2·626-0·00008\theta$. G. Quincke's values[9] for the **capillary constant** of molten sodium bromide is $a^2=4·08$ sq. mm.; and potassium bromide, $a^2=4·49$. The value for the **surface tension** of molten sodium bromide is 49·0 dynes per cm., and for potassium bromide, 48·4 dynes per cm. J. M. Jäger's values for the sp. gr., the surface tension (ergs per cm.), and the mol. surface energy (ergs per sq. cm.) are indicated in Table XXV. T. W. Richards and G. Jones' value for the compressibility of sodium bromide at 20° between 100 and 500 atm. is $5·1\times10^{-6}$ megabars. and of potassium bromide $6·2\times10^{-6}$ megabars. W. C. Röntgen and J. Schneider studied the **compressibility** of soln. of lithium, sodium, and potassium bromides; F. Pohl, sodium and potassium bromide; and O. Schmidt of lithium bromide—*vide* ammonium iodide.

TABLE XXV.—SPECIFIC GRAVITIES AND SURFACE TENSIONS OF THE MOLTEN ALKALI BROMIDES.

Temp.		Surface tension.	Sp. gr.	Mol. surface energy.	Temp. coeff. per deg.
NaBr	760·9° . .	105·8	2·320	1325·0	0·53
	1165·7° . .	78·0	1·912	1112·0	0·53
KBr	775° . .	85·7	2·086	1270·2	0·76
	920° . .	75·4	1·970	1161·0	0·76
RbBr	729° . .	87·7	2·656	1377·7	0·77
	1121° . .	60·6	2·226	1071·0	0·77
CsBr	657·7° . .	81·8	3·116	1366·4	0·90
	970·6° . .	62·7	2·695	1153·7	0·67

The **melting point** of lithium bromide is 442°, according to W. Ramsay and N. Eumorfopoulos[10]—this value seems to be much too low, for T. Carnelley gives 547° ± 5°; G. Kellner, 552°; and G. Scarpa, 550°. For sodium bromide, V. Meyer and W. Riddle gave 757·7°; W. Ramsay and N. Eumorfopoulos, 733°; T. Carnelley, 708°–712°; N. S. Kurnakoff and S. F. Schemtschuschny, 768°; J. MacCrae, 761°; G. Scarpa, 776°; G. Kellner, 742°; O. Ruff and W. Plato, 765°; and K. Hüttner and G. Tammann, 749°. For potassium bromide, V. Meyer and W. Riddle give 722°; and T. Carnelley, 703°, and, according to the latter, the salt freezes at 685°; K. Hüttner and G. Tammann gave 740°; for the m.p. M. Amadori and G. Pampanini, 740°; P. de Cesaris, 730°; G. Scarpa, 760°; G. Kellner, 730°; N. S. Kurnakoff and S. F. Schemtschuschny, 790°; O. Ruff and W. Plato, 750°. T. Carnelley gives the m.p. of rubidium bromide as 683°. Potassium bromide,

says M. Berthelot,[11] volatilizes at a high temp., and its **boiling point**, according to J. McCrae, is 745°. L. H. Borgström gives 1455° for the b.p. of sodium bromide, and 1435° for potassium bromide. G. Bartha gave 725° for the b.p. of sodium bromide in the cathode light, and 680° for potassium bromide. According to R. Bunsen, potassium bromide volatilizes 0·487 times and sodium bromide 1·727 times as fast as the same quantity of sodium chloride in the hottest part of the Bunsen flame. Anhydrous lithium bromide gives off a little bromine when heated to its m.p., sodium and cæsium bromides do not. According to G. Scarpa, in the binary system LiOH—LiBr, there is a eutectic at 275° with 45 mol. per cent. of the hydroxide, and an arrest at 310° corresponding with unstable **lithium trihydroxybromide,** 3LiOH.LiBr. The systems NaOH—NaBr and KOH—KBr are completely miscible in the liquid state; in the former case there is a eutectic at 260° with 80 mol. per cent. of NaOH; and in the latter case, at 205° with 90 mol. per cent. of KOH. The former is a simple eutectic, the latter gives solid soln. of two kinds with a miscibility break. The transformation points of the alkali hydroxides are rapidly lowered by the corresponding bromides. A. von Weinberg obtained 45·7 Cals. for the **heat of sublimation** of sodium bromide, and 45·2 Cals. for that of potassium bromide; and A. Reis obtained 55 and 50 Cals. respectively for sodium and potassium bromides, and between 15 and 35 Cals. for lithium bromide.

The **specific heat** of sodium bromide is 0·13842 and of potassium bromide 0·11322 between 16° and 98°, according to H. V. Regnault.[12] J. N. Brönsted gives for the sp. ht. of the alkali bromides between 0° and 20°:

	NaBr	KBr	RbBr	CsBr
Sp. ht.	0·1176	0·1031	0·0743	0·0582
Mol. ht.	12·10	12·27	12·29	12·38

F. Koref obtained for the sp. ht. and mol. ht. of sodium bromide between −191·4° and −82·0°, respectively 0·1014 and 10·44; and between 0° and −76·4°, 0·1170 and 12·04. Similarly, for potassium bromide between −190·8° and −82·1°, 0·0911 and 10·84; and between 0° and −77·5°, 0·1025 and 12·20. W. Nernst gives for the mean atomic heat of potassium bromide at 78·7° K., 9·48; and at 89·2° K., 10·05. G. N. Lewis and G. E. Gibson estimate the increase of entropy from −273° to 25° as 22·4. The **heat of formation** of lithium bromide, according to A. Bodisco,[13] $Li+Br_{liq.}=LiBr_{solid}+80·2$ Cals.; $Li+Br_{liq.}=LiBr_{soln.}+91·5$ Cals.; $Li+Br_{gas}=LiBr_{solid}+83·9$ Cals.; $Li+Br_{gas}=LiBr_{soln.}+95·2$ Cals. The heat of formation of sodium bromide from its elements is 85·77 Cals.; and of potassium bromide: $K+Br_{solid}=KBr_{solid}+96·4$ Cals. According to N. N. Beketoff, the heat of formation of cæsium bromide is 99·8 Cals. The **heat of solution** of lithium bromide is LiBr+Aq=11·35 Cals., according to A. Bodisco; sodium bromide, −0·29 Cal. (M. Berthelot), −0·19 (J. Thomsen); for potassium bromide, at 18°, −5·08 Cals. (J. Thomsen), and −545 Cals. at 10·6° (M. Berthelot). The heat of soln. Q of a mol. of potassium bromide in 200 mols. of water varies with temp. according to the equation $Q=5·240+0·038(\theta-15)$ Cals. N. N. Beketoff gives the heat of soln. of cæsium bromide as −6·3 Cals. The **heat of neutralization** is: NaOH + HBr = 13·6 Cals.; $HBr_{soln.} + \frac{1}{2}K_2O_{soln.} = KBr + H_2O + 13·5$ Cals.; $HBr_{solid}+NaOH_{solid}=NaBr_{solid}+H_2O_{solid}+34$ Cals., and for potassium hydroxide, 41·7 Cals. Potassium bromide is nearly twice as soluble as the corresponding chloride in water at 0°. A. von Weinberg obtained 150·1 Cals. for the heat of dissociation of lithium bromide; 140·1 Cals. for sodium bromide; 144·2 Cals. for potassium bromide; 145·0 Cals. for rubidium bromide; and 145 8 for cæsium bromide.

The **solubilities** of the alkali halides in 100 grms. of water are:

	0°	10°	20°	40°	60°	80°	1000°
LiBr . . .	143	161	177	202	224	245	266
NaBr . . .	79·5	84·5	90·3	105·8	117·0	119·0	121·0
NH_4Br . . .	—	66·2	74·0	87·5	101·0	115·0	128·2
KBr . . .	53·5	59·5	65·2	75·5	85·5	95·0	104·0

The data for lithium bromide are by P. Kremers,[14] and the data for sodium bromide by L. C. de Coppet—A. Étard's data are much lower than L. C. de Coppet's. The solubility of sodium bromide in 100 grms. of water is 57·5 (A. Étard), 71·4 (L. C. de Coppet) at −20°; 116 (A. Étard); 124 (L. C. de Coppet) at 120°; and 118 (A. Étard) at 140°. F. Guthrie gives for sodium bromide 67·5 at −28°; 70 at −24°; 71·4 at −20°; and 75·1 at −10°. L. C. de Coppet was unable to make a satisfactory interpolation formula for the solubility S of sodium bromide. A. Étard gives $S=40+0·01746\theta$ grms. per 100 grms. of water between 20° and 40°; and $S=52·3\pm0·0125\theta$ between 40° and 150°. Values for the solubility of potassium bromide have been obtained by A. Meusser, A. Étard, W. A. Tilden and W. A. Shenstone, and by L. C. de Coppet. A. Meusser gives 46·7 for −10°; 109·5 for 110°; 120·9 for 140°; and 145·6 for 181°. L. C. de Coppet gives the interpolation formula for the solubility S between −13·4° and 110° of potassium bromide at θ° as $S=54·43+0·5128\theta$ grms. of salt per 100 grms. of water; and A. Étard gives $S=34·5+0·2420\theta$ between 0° and 40°, and $S=41·5+0·1378\theta$ between 30° and 120°. The values for rubidium bromide by E. Rimbach are:

	0·5°	5·0°	16·0°	39·7°	57·5°	113·5°
RbBr	89·6	98·0	104·8	131·85	152·47	205·21

L. Reissig gives the solubility of rubidium bromide as 98 grms. in 100 grms. of water at 5°; and 105 grms. at 16°. J. N. Brönsted measured the solubility of the alkali halides in aq. soln. of *potassium hydroxide* at 20°. For the solubility of potassium bromide in aq. and nitrobenzene soln. of bromine, *vide* bromine.

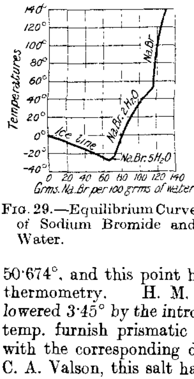

FIG. 29.—Equilibrium Curve of Sodium Bromide and Water.

Lithium bromide separates from its aq. soln. in very deliquescent crystals, and it forms different hydrates which are determined by the temp. of crystallization.[15] With cold soln., fine needle-like crystals of **trihydrated lithium bromide,** $LiBr.3H_2O$, melting at 3·5°, are formed; at 4° these pass into prismatic crystals of **dihydrated lithium bromide,** $LiBr.2H_2O$, melting at 44°; the dihydrated salt passes into **monohydrated lithium bromide** at 44°; and at 159° into the anhydrous salt. W. Meyerhoffer's[16] solubility curve of sodium bromide is shown in Fig. 29. The transition point of **dihydrated sodium bromide,** $NaBr.2H_2O$, to the anhydride is 50·674°, and this point has been suggested by T. W. Richards as a fixed-point in thermometry. H. M. Dawson and C. G. Jackson found the transition point lowered 3·45° by the introduction of urea. Aq. soln. of sodium bromide at ordinary temp. furnish prismatic monoclinic crystals of the dihydrated salt, isomorphous with the corresponding dihydrated sodium iodide. According to P. A. Favre and C. A. Valson, this salt has a sp. gr. of 2·176±0·003; according to R. Krickmeyer, 2·17(20°/4°); and according to M. Berthelot, the heat of formation is $NaBr+2H_2O=NaBr.2H_2O+4·15$ Cals. The dihydrated salt is stable over the range from 50·674° down to −24° when **pentahydrated sodium bromide,** $NaBr.5H_2O$, is formed, and the range of stability of this salt is small—between −24° and −48°. The eutectic temp. is −28°. The increase in the solubility of the anhydrous salt with a rise of temp. is smaller than with the dihydrated salt, and this corresponds with the smaller heat of soln. of the latter. No hydrated bromides of potassium, rubidium, or cæsium are known. One way of expressing this is to say that the electro-affinity of the potassium ion is greater than is the case with the sodium ion, and consequently the tendency to hydration is less. According to F. Guthrie and F. Rüdorff, the eutectic temp. with potassium bromide is −13°, and the mixture then contains 47 grms. of the salt in 100 grms. of water.

The **specific gravities** of soln. containing n grms. of lithium bromide per 100 grms. of water at 19·5° have been determined by P. Kremers,[17] and recalculated

by G. T. Gerlach similarly for sodium bromide at 15°; and of potassium bromide at 19·5°:

n	5	10	15	20	25	30	35	40	50	55
LiBr	1·035	1·072	1·113	1·156	1·204	1·254	1·309	1·368	1·500	1·580
NaBr	1·040	1·080	1·125	1·174	1·266	1·281	1·344	1·410	1·565	—
KBr	1·037	1·075	1·116	1·159	1·207	1·256	1·309	1·366	1·430	—

M. le Blanc and P. Rohland give the sp. gr. of a 6·60 per cent. soln. of rubidium bromide at room temp. as 1·0525; and of a 14·36 per cent. soln. as 1·1225. G. P. Baxter has measured the sp. gr. of soln. of the five alkali bromides and compared the observed mol. vol. of the solids with those computed from the at. vol. of the elements, and with the mol. vol. of the salts in soln. C. Forch's values[18] for the **coefficient of cubical expansion** a of aq. soln. of 59·5 grms. of potassium bromide are 0·000067 (0°–5°), 0·000128 (5°–10°), and 0·000387 (35°–40); for 119 grms. of potassium bromide per litre, 0·000140 (0°–5°), 0·000184 (5°–10°), and 0·000406 (35°–40°); and for 2·38 grms. per litre, 0·000241 (0°–5°), 0·000269 (5°–10°), and 0·000444 (35°–40°).

The **coefficient of thermal expansion** (linear) for crystals of potassium bromide, by H. Fizeau, is a=0·000042007 at 40°. The coeff. of cubical expansion of crystals of the alkali bromides, by G. P. Baxter and C. C. Wallace, are:

	NaBr	KBr	RbBr	CsBr
0°–25°	0·000122	0·000112	0·000113	0·000141
25°–50°	0·000119	0·000125	0·000101	0·000137

The **diffusion coefficient**[19] of sodium bromide is 0·86 at 10° for soln. of sodium bromide containing 2·9 mols. per litre; and for *N*-soln. of potassium bromide, 1·13 per sq. cm. per day. The **capillary constant**[20] of fused sodium bromide is a^2=4·08, and potassium bromide, a^2=4·49 sq. mm. The **surface tensions** are respectively 49·0 and 48·4 dynes per cm. W. Herz and G. Anders[21] measured the viscosities of soln. of alkali bromides; and F. Körber the effect of press. on the viscosities as indicated in Table XIX.

The **boiling point** of a sat. soln. of sodium bromide is 121°; and of potassium bromide, 112°. The b.p. of water is raised 0·120° with the soln. of 1·35 grms. of sodium bromide (A. Schlamp),[22] and 1·872°, with 17·92 grms. of the same salt (W. Landsberger) per 100 grms. of water. Similarly, with 2·614 grms. of potassium bromide per 100 grms. of water, L. Kahlenberg observed a rise of 0·206°, and with 50·14 grms., 7·754°. The mol. rise of the b.p. of sodium bromide soln. increases with increasing conc. from 0·92° to 1·076° and of potassium bromide from 0·94° to 1·13° in the examples quoted. This is just the opposite to what would be expected if the ionization decreased with increased conc. Hence it is assumed that the hydration of the salt in soln. marks the effect produced by the ionization of the salt *per se*. G. Tammann[23] has measured the lowering of the **vapour pressure** of water at different temp. by soln. of lithium, sodium, and potassium bromides. The mol. lowering of the **freezing point** of aq. soln. of lithium bromide, determined by W. Biltz, is 0·292° with 0·07845 mol. of LiBr per 1000 grms. of water, and 3·631° with 0·9138 mol. H. Jahn's values for the mol. lowering of the f.p. of soln. of sodium bromide are 3·444° for 0·3053*N*-soln. of NaBr; and 3·602° for 0·02542*N*-soln. W. Biltz and H. Jahn's[24] have likewise found values for potassium bromide where for soln. with 0·363 grm. of the salt per 100 grms. of water the lowering of the f.p. is 3·61°, and with 8·101 grms. of salt, 3·30°. The depression of the f.p. of both the chlorides and bromides is greater with conc. soln. than corresponds with the degree of ionization deduced from conductivity measurements, and this fact is cited as evidence of the formation of hydrates, or, according to H. C. Jones and J. N. Pearce, as evidence of the formation of hydrated ions.

The **specific heat** of a 3·2 per cent. soln. of potassium bromide (*i.e.* one eq. per 400 eq. of water) is 0·962 at 18° according to J. Thomsen[25]; and J. C. G. de Marignac, between 20° and 51°, gives the sp. ht. 0·7691 for soln. containing 2 eq. of KBr per

50 eq. of water, H_2O; 0·8643 per 100 eq. of water; and 0·9250 per 200 eq. of water; the corresponding values for sodium bromide are respectively 0·8092, 0·8864, and 0·9388. According to G. Jäger,[26] the **thermal conductivity** of a 40 per cent. soln. of potassium bromide, is 81·1 (silver unity); 40 per cent. soln. of sodium bromide, 88·9; and 20 per cent. soln. of sodium bromide, 93.

H. Topsöe found the **refractive indices** of crystals of potassium bromide to be 1·5546 for the *C*-line; 1·5593 for the *D*-line; 1·5715 for the *F*-line; and 1·5814 for the *H*-line. Similar results were obtained by M. Sprockhoff, and for rubidium bromide, 1·5483 for the *C*-line; 1·5528 for the *D*-line; and 1·5646 for the *F*-line. For the cæsium bromide, M. Sprockhoff obtained 1·6924 for the *C*-line; 1·6984 for the *D*-line; and 1·7126 for the *F*-line. The refractive index μ of soln. of lithium, sodium, and potassium bromides have been determined by G. P. Baxter; and for potassium bromide soln. by A. H. Borgesius,[27] at 18° for the *D*-line. The fractional increase in the refractive index $(\mu-\mu_0)/w$ of soln. containing w per cent. of the salt per litre, is

w	2·9210	1·4705	0·7370	0·3710	0·1840
$(\mu-\mu_0)w$.	0·001204	0·001197	0·001196	0·001191	0·001180

M. le Blanc gave tbe refractive indices of soln. of potassium and rubidium bromides as 1·5593 and 1·5533 respectively, when the densities are 2·738 and 3·314 respectively. Hence the refraction eq. of potassium bromide by Gladstone and Dale's formula is therefore 24·32; and by Lorentz and Lorenz's formula 14·05; the corresponding values for rubidium bromide are 27·62 and 15·98. The mol. refractions of potassium bromide in soln. by the two formulæ are respectively 25·11 and 14·70; and of rubidium bromide in soln., 27·85 and 16·33. The mol. refractions of these salts are therefore greater in soln. than in the solid form. Crystals of potassium bromide, says H. Marbuch, exhibit optical activity. A. S. Newcomer found that sodium chloride was the only salt relatively soluble and yet capable of emitting fluorescent rays in the mid-ultra-violet region of the spectrum under the influence of **X-rays.**

W. Ostwald's values [28] for the eq. **electrical conductivity** λ of soln. of sodium bromide and of potassium bromide, when a mol. of the salt is dissolved in v litres of water, at 25°, are:

v	32	64	128	256	512	1024
NaBr, λ	115·0	118·2	121·3	124·2	126·4	127·8
KBr, λ	137·2	140·9	145·1	148·1	148·2	150·5

From their values of the electrical conductivities of soln. at 18°, F. Kohlrausch and H. von Steinwehr calculate the degree of ionization of soln. containing 0·0001 mol. of KBr per litre to be 99·1 per cent., and for soln. with 0·5 mol. of KBr per litre, 79·6 per cent. O. Gropp measured the effect of temp. on the conductivity of liquid and frozen soln. of lithium, sodium, and potassium bromides. F. M. Jäger and B. Kampa measured the mol. conductivity, μ, of potassium bromide at $\theta°$ between 745·2° and 868·6°, and found $\mu=90{\cdot}09+0{\cdot}1906\ (\theta-750)$. S. Arrhenius gives for the temp. coeff. of the conductivity between 18° and 52°, for 0·001, 0·01, 0·1, and 0·5 normal soln., 0·0231, 0·0228, 0·0225, and 0·0210 respectively; he also computes the **heat of ionization** in $\frac{1}{10}N$-soln. of KBr at 35° to be —425 cals. P. Bogdan [29] gives the **transport number** 0·604 at 18° for soln. between 0·0008 and 0·15N-NaBr; and 0·504 at 18° for 0·034 to 0·011N-soln. of KBr. For the effect of press. on the electrical properties, *vide* alkali chlorides. A. Reis gave for the **free energy** for the separation of the ions of KBr, 155 kgrm. cals. per mol.; NaBr, 171; LiBr, 167; and HBr, 315. A. Heydweiller gave 2·85 and 4·70 for the **dielectric constants** of powdered and compact potassium bromide.

A. Ditte [30] found the solubility of sodium or potassium bromide to be decreased by the presence of the corresponding hydroxide in the same soln. Thus, the water solubility of sodium bromide at 17° falls from 91·38 to 68·85 per 100 grms. of water in the presence of 9·24 grms. of sodium hydroxide, and to 24·76 in the presence of

54·52 grms. of the hydroxide ; similarly, the water solubility of potassium bromide falls from about 63 to 43·36 per 100 grms. of water in the presence of 11·35 grms. of potassium hydroxide, and to 3·24 in the presence of 80·69 grms. of the same hydroxide. A. Étard and C. Touren measured the solubility of potassium bromide in aq. soln. of potassium chloride, iodide, and nitrate. The solubility was in all cases decreased as the proportion of the second salt in soln. increased.

A. E. Taylor[31] found the solubility of potassium bromide per 100 grms. of aq. *ethyl alcohol*, at 30°, to be reduced as the proportion of alcohol increased, falling from 71·30 with water, as solvent to 56·4 with a 20 per cent. alcohol ; to 44·95 with 40 per cent. alcohol ; to 32·50 with 60 per cent. alcohol : and to 8·80 with 90 per cent. alcohol ; while C. A. L. de Bruyn obtained a solubility (25°) of 0·13 with absolute ethyl alcohol. Absolute *methyl alcohol* dissolved 1·51 grms. of potassium bromide at 25° ; and *propyl alcohol* 0·055 grm. at room temp. Similarly, P. Rohland, C. A. L. de Bruyn, and J. M. Eder have shown that 100 grms. of methyl alcohol (sp. gr. 15°, 0·799) dissolved 21·7 grms. of sodium bromide, and absolute methyl alcohol, 17·35 grms. The same amount of ethyl alcohol (sp. gr. 15°, 0·810) at 19·5° dissolves 7·14 grms. of sodium bromide, and absolute ethyl alcohol at 15°, dissolves 6·3 grms. of dihydrated sodium bromide ; likewise with propyl alcohol 100 c.c. (sp. gr. at 15°, 0·816) at room temp. dissolve 2·01 grms. of sodium bromide, 100 grms. of absolute *ethyl ether* dissolve 0·08 grm. of sodium bromide at 15°. H. C. Jones found that the mol. wt. of potassium, sodium, and ammonium bromides in methyl and ethyl alcohol when determined by the b.p. method correspond with an ionization of approximately 50 per cent. in the former solvent, and 25 per cent. with the latter. W. Herz and M. Knoch found that at 25°, the water solubility of potassium bromide fell from 57·32 grms. of the salt to 43·67 grms. per 100 c.c. of soln. when 120 c.c. of the solvent had 20 c.c. of *acetone* and with 90 c.c. of acetone to 1·20 grms. of potassium bromide. The corresponding sp. gr. of these three soln. were 1·3793, 1·2688, and 0·8340. S. W. Serkov found evidence of the formation of complexes in his study of acetone soln. of lithium bromide. Likewise, the solubility per 100 c.c. of a 13·28 per cent. soln. of *glycerol* was 52·91 grms. of potassium bromide, and the soln. had a sp. gr. 1·3704 ; with 100 c.c. of a 100 per cent. soln. of glycerol, 20·56 grms. of potassium bromide and the sp. gr. of the soln. was 1·3691 ; there is a minimum 1·3580 in the sp. gr. with a 54·23 per cent. glycerol, when 100 c.c. of the soln. has 36·98 grms. of salt. P. Walden found 100 c.c. of a sat. soln. in *furfural* ($C_4H_3O.COH$), at 25°, contains 0·139 grms. of potassium bromide. M. Stuckgold found a litre of *ethyl urethane*, at 60°, dissolved 0·493 mol. of sodium bromide, 0·032 of potassium bromide, and 0·034 of rubidium bromide.

According to W. Herz and G. Anders,[32] sat. soln. of potassium bromide in water and methyl alcohol at 25° contain respectively 4·708 and 0·142 mols. per litre ; the soln. have respectively the sp. gr. 1·37927 and 0·80493 referred to water at 4° ; the relative **viscosities**, 1·062 and 0·697 ; the relative eq. conductivities 91·3 and 57·9 ; and the specific conductivities, 0·4297 and 0·00825. P. Dutoit and A. Levier have measured the conductivities of soln. in acetone, and hence inferred that in this solvent potassium bromide is much less ionized than potassium iodide.

Liquid *sulphur dioxide*, says P. Walden,[33] readily dissolves sodium and potassium bromides, and C. J. J. Fox has shown that at 25° the solubility S of sulphur dioxide in soln. of sodium bromide, unlike sodium chloride, is greater than it is in water, *viz.* 32·76. Thus for soln. of these salts of normality N, the solubility of sulphur dioxide is :

N-soln.	0·5	1·0	1·5	2·0	2·5	3·0
NaCl, S	32·46	32·25	31·96	31·76	31·51	31·36
NaBr, S	33·76	34·54	35·27	36·26	36·84	37·74

Hence the solubility of sulphur dioxide in sodium chloride soln. is less than it is in water, and in sodium bromide soln. greater ; and the difference is the greater

the greater the amount of halide in soln. Similar results were obtained with potassium bromide or sodium bromide. P. Walden found the electrical conductivity λ of a soln. of a mol. of potassium bromide in 14·6 litres of liquid sulphur dioxide to be 30·9, and in 71·5 litres, 35·9. S. Tolloczko showed also that the lowering of the f.p. of soln. of potassium bromide in *antimony trichloride* increased with dilution, showing that the salt may be more and more ionized in that solvent.

According to F. C. Franklin and C. A. Kraus,[34] liquid ammonia readily dissolves sodium and potassium bromide. The change in the vap. press., p, of normal soln. of ammonia containing C mols. of lithium, sodium, or potassium bromide per litre at 25° is reduced :

C	0·0	0·5	1·0	1·5
LiBr, p	13·45	13·43	12·94	12·35 mm.
NaBr, p	13·45	13·95	14·69	15·10 mm.
KBr, p	13·45	14·14	14·89	15·70 mm.

Lithium bromide also, like lithium chloride, absorbs considerable amounts of ammonia, forming a series of analogous ammino-compounds. **Lithium monammino-bromide,** $LiBr.NH_3$, is formed by passing ammonia gas over lithium bromide, heated above 95°, or else by heating one of the higher ammino-compounds above this temp. It forms colourless crystals melting at 97° ; it remains liquid at 170°, but above this temp. it loses all its ammonia. The dissociation press. is 730 mm. at 95·5°, or 806 mm. at 97·5° ; the thermal value of absorption is 13·293 Cals. The heat of soln. is 6·857 Cals. **Lithium diammino-bromide,** $LiBr.2NH_3$, is formed between 87° and 95° ; it has a dissociation press. of 655 mm. at 85°, and 847 mm. at 90·2°. The heat of formation is 25·937 Cals., and the heat of absorption for the last mol. of ammonia is 12·64 Cals. The heat of soln. is 3·013 Cals. **Lithium triammino-bromide,** $LiBr.3NH_3$, is formed between 71·5° and 87° ; its dissociation press. is 636 mm. at 67°, and 807 mm. at 71·8°.[35] The heat of formation is 37·63 Cals., and the heat of absorption for the last mol. of ammonia is 11·53 Cals. The heat of soln. is 0·287 Cal. **Lithium tetrammino-bromide,** $LiBr.4NH_3$, is formed as a white, voluminous powder at −18° ; its dissociation press. at 56° is 681 mm., and at 58·25°—F. Ephraim gives 53·8°—760 mm. The heat of formation is 48·098 Cals., the heat of absorption for the last molecule of ammonia is 10·64 Cals. The heat of soln. is −1·548 Cals.

The chemical properties of the alkali bromides.—According to A. Potilitzin,[36] potassium bromide at a red heat is but slightly attacked by oxygen ; but as H. Schulze has shown, the attack is more vigorous if acid anhydrides—P_2O_5, SO_3, etc.—be also present. A. Gorgeu showed that potassium bromide is decomposed rather more easily than the chloride when fused with clay or with silica, although the attack by boric oxide or silica is not vigorous. Potassium bromate, says O. Henry, is formed when the bromide is fused with the chlorate. According to W. Reinige, when a soln. of potassium permanganate and potassium bromide is boiled, there is very little action, but if sulphuric acid be present, some bromine is evolved. The action of sulphuric acid has been previously discussed in connection with the preparation of hydrogen bromide by the action of this acid on the alkali bromide. According to H. L. Snape,[37] carbon tetrachloride and phosphorus trichloride have no action on potassium bromide, while a little potassium chloride is formed when the bromide is heated with arsenic trichloride or sulphur monochloride. H. L. Wheeler prepared hexagonal crystals of compounds of arsenic tribromide with cæsium and rubidium bromides—*e.g.* $3CsBr.2AsBr_3$, and $3RbBr.2AsBr_3$. J. Nicklés also states that the alkali halides unite with the respective bromides of arsenic, antimony, and bismuth. F. Sestini and F. Rüdorff have studied the compounds of arsenious oxide with potassium halides, and they made $KBr.2As_2O_3$, etc. The compounds $CsBr.As_2O_3$ and $RbBr.As_2O_3$ also form well-defined hexagonal crystals. Many other double compounds with the metal halides have been reported : H. L. Wells' $2RbBr_2.PbBr_2.\frac{1}{2}H_2O$ and $RbBr.2PbBr_4$;

H. L. Wheeler's $2KBr.TeBr.2H_2O$; $2RbBr.TeBr_4$; and $2CsBr.TeBr_4$; A. Chassevant's series, $MCl_2.LiCl.3H_2O$, where M denotes an atom of copper, manganese, iron, cobalt, or nickel ; J. F. Aloy's $UCl_4.2LiCl$.

A. J. Balard [38] knew that chlorine will displace bromine from the bromides when in soln., and the result has been shown to be in conformity with the thermal data. The reaction is utilized for detecting traces of bromides in the presence of chlorides. The action does not occur, says F. W. Küster, if the chlorine and potassium are quite free from moisture. Iodine does not displace bromine from the bromides, although hydriodic acid evaporated with potassium bromide forms potassium iodide and free bromine ; the displacement with hydrochloric acid is incomplete and partial. In the absence of water, the attack on potassium bromide at a red heat by hydrogen chloride is feeble. Hypochlorous acid decomposes potassium bromide, forming bromate, chlorine, and free bromine. Dry potassium bromide absorbs about twice its volume of hydrogen bromide, forming traces of what M. Berthelot [39] regards as a **potassium hydrobromide,** say, $KBr.HBr$, or $KHBr_2$. M. Berthelot found a little hydrogen is evolved when the potassium hydrobromide is heated with mercury. The solubility of potassium bromide in water is increased by the addition of bromine ; for moderate conc. about 0·5 mol. additional bromide is dissolved for each mol. of bromine added to the water. The limit of the solvent capacity of the water was not reached at bromine conc. of more than 2000 grms. per litre of soln. ; for example with a soln. of the composition by weight—water 5·4 per cent., bromide 15·1 per cent., bromine 79·5 per cent.

In 1828 C. Löwig noticed that a conc. soln. of potassium bromide dissolves a large quantity of bromine, forming a dark-brown liquid. The heat of soln. of a mol. of bromine in the mixture $5(KBr+14H_2O)$ is 3·53 Cals., and in $6(KBr+110H_2O)$, 2·7 Cals. The soln. can be diluted with water without the separation of bromine, but the excess of bromine slowly escapes on exposure to the air or when the soln. is heated. The evidence indicating the formation of a polybromide has already been discussed. If equimolecular parts of potassium bromide and bromine be left some days in a sealed tube, orange-coloured crystals of what M. Berthelot regards as partially dissociated **potassium tribromide,** KBr_3, are formed. The heat of formation, says M. Berthelot, is $KBr_{solid}+Br_{2liq.}=KBr_3+2{\cdot}94$ Cals. ; or $KBr_{solid}+Br_{2gas}KBr_3+10{\cdot}3$ Cals. When a mol. of cæsium bromide is mixed with a gram-atom of bromine, in a soln. containing three parts of water to one part of salt, and the whole vigorously heated until the colour of the bromine disappears, crystals of **cæsium tribromide,** $CsBr_3$, separate from the soln. on cooling. P. Ephraim found the dissociation press. of cæsium tribromide to be 66 mm. at 91·8° ; 387 mm. at 131° ; 655 mm. at 143·5° ; and 760 mm. at 147·5°. H. L. Wells and H. L. Wheeler [40] also prepared **rubidium tribromide,** $RbBr_3$, by a similar process to that employed for the cæsium salt. F. Ephraim found its dissociation press. to be 87 mm. at 63° ; 412 mm. at 93·2° ; 608 mm. at 101·5° ; and 760 mm. at 105·5°. A series of dichlorobromides, $MBrCl_2$, and a series of chlorodibromides, MBr_2Cl, have been prepared. The m.p., temp. of whitening by decomposition, and the axial ratios of the rhombic crystals of the alkali tribromides, and chlorobromides are indicated in Table XXVI.

TABLE XXVI.—THE ALKALI TRIBROMIDES AND CHLOROBROMIDES.

	M.p.	Decomposition by "whitening" test.	Axial ratios $a : b : c$.
$RbBr_3$	whitens	140°	0·6952 : 1 : 1·1139
$CsBr_3$	180°	160°	0·6873 : 1 : 1·0581
$RbBrCl_2$	whitens	140°	0·7146 : 1 : 1·1430
$CsBrCl_2$	205°	160°	0·7186 : 1 : 1·1237
$RbBr_2Cl$	76° (?)	110°	0·70 0 : 1 : 1·1269
$CsBr_2Cl$	191°	150°	0·6990 : 1 : —

F. Ephraim found the dissociation press. of **cæsium chlorodibromide,** $CsBr_2Cl$, is 15 mm. at 54° ; 317 mm. at 104° ; 624 mm. at 120° ; and 760 mm. at 124°. Similarly, for **rubidium chlorodibromide,** $RbBr_2Cl$, the dissociation press. is 30 mm. at 18° ; 240 mm. at 62° ; 565 mm. at 100·1° ; and 760 mm. at 105·5°. The dissociation press. of **cæsium dichlorobromide,** $CsBrCl_2$, is 45 mm. at 79° ; 228 mm. at 112° ; 612 mm. at 132·5° ; and 760 mm. at 138°. The dissociation press. of **rubidium dichlorobromide,** $RbBrCl_2$, is 20 mm. at 17° ; 235 mm. at 72·5° ; 699 mm. at 91·5° ; and 760 mm. at 93°.

H. L. Wells and H. L. Wheeler found that when cæsium bromide is shaken up with a large excess of bromine there is no separation of the tribromide as is the case when the theoretical amount of bromine is used. The colour of the soln. is lighter than bromine, and the soln. deposits dark-red crystals when evaporated spontaneously at 0°. Analyses agree with the formula : **cæsium pentabromide,** $CsBr_5$. The crystals are rather unstable.

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§ 18. Ammonium Bromide

Ammonium bromide is formed by the direct union of the two gases; and by the neutralization of hydrobromic acid with ammonia. C. F. Schönbein [1] made it along with the hypobromite (*q.v.*) and bromate, when ammonia is treated with bromine water until it reacts alkaline—some nitrogen is formed at the same time.

Into a flask containing 220 c.c. of 30 per cent. aqua ammonia cooled by a freezing mixture, slowly run 75 c.c. of bromine from a dropping funnel with its stem drawn out to a fine point. The liquid should be continuously agitated when the ammonia is being added, and it should also remain strongly ammoniacal when all the bromine has been introduced. Warm the mixture to drive off the excess of ammonia, and evaporate until the liquid crystallizes. The crystals are dried in a porcelain dish over a hot plate. About 220 grms. of the required salt can be so obtained.

As with the corresponding chloride ammonium bromide is also formed in other reactions—*e.g.* W. Muthmann and E. Seitter found that thiotrithiazyl bromide, S_4N_3Br, is largely converted into ammonium bromide when boiled with water. J. Knobloch recommended preparing this salt by first making a mixture of ferrous and ferric bromides by the action of bromine on iron; then precipitating the iron with milk of lime, and decomposing the calcium bromide with ammonium sulphate. The clear liquor was freed from the soluble calcium sulphate by treatment with barium bromide, and the calcium and barium removed by treatment with ammonium carbonate. The filtrate was acidified with hydrobromic acid and evaporated. C. Rice recommended making ammonium bromide by double decomposition with ammonium sulphate.

The **crystals** of ammonium bromide agree in all respects with those of ammonium chloride. They belong to the cubic system, and the crystals obtained from aq.

soln. are probably pentagonal icositetrahedrons. According to A. Johnsen[2] and J. W. Retgers, cubes are obtained from soln. containing urea, chromic chloride, or lead chloride or bromide, and trapezohedra with ferric chloride. A. Fock found ammonium bromide forms a limited range of mixed crystals with potassium bromide to 40 per cent. of ammonium bromide, 60 per cent. potassium bromide, and to 98·5 per cent. ammonium and 1·5 potassium bromide. **X-radiograms** of the form of ammonium bromide stable at 20°, by G. Bartlett and I. Langmuir, show that the space lattice is a centred cube with like ions $3·988\times10^{-10}$ cm. apart, and unlike ions $3·453\times10^{-10}$ cm. apart; while the form stable at 250°, has a simple cubic lattice with like ions $4·88\times10^{-10}$ cm. apart, and unlike ions, $3·45\times10^{-10}$ cm. apart. R. C. Wallace found that ammonium bromide undergoes a transformation into a less polymerized form at 109°, analogous to that which occurs with ammonium chloride at 159°. F. E. C. Scheffer obtained a transition between 124° and 147° without a catalyst, but with glycerol as a catalyst, between 137·3° and 139·5°; no discontinuity in the vap. press. p of sat. soln. $\log p=-1926·6T^{-1}+6·8302$ was observed corresponding with this transition point. The two solubility curves—the one below the transition point $\log x=-372·7T^{-1}+0·31978$; and the one above the transition point $\log x=-293·7T^{-1}+0·12727$, where x denotes the mol. fraction of NH_4Br—intersect at 137·4°. P. W. Bridgman gives 137·8° for the transition temp., and the effect of press. on this temp. is indicated in Fig. 30 and Table XXVII.

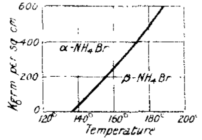

FIG. 30.—Effect of Pressure on the Transition Temperature of Ammonium Bromide.

TABLE XXVII.—THE TRANSITION TEMPERATURE OF AMMONIUM BROMIDE.

Press.	Transition temp.	Change of vol. c.c. per gram.	Latent heat kgrm.-metres per gram.
1	137·8°	0·0647	3·32
100	146·0°	0·0652	3·28
500	181·9°	0·0659	3·09
700	202·0°	0·0655	2·99

The reported values for the **specific gravity**[3] of this salt range from C. H. D. Bodeker's 2·266 (10°) to J. S. Stas' 2·456. J. M. Eder gave 2·3270 (15°) for the crystallized salt, and 2·3394 (15°) for the sublimed salt. W. Biltz has studied the mol. vol. of this salt.

Ammonium bromide volatilizes without fusion or decomposition. Ammonium bromide sublimes without giving any bromine; but the vapour given off at the beginning of the sublimation reacts alkaline, and at the end of the operation, acid. The **vapour density** obtained by H. St. C. Deville and L. Troost[4] is 1·67 at 440°, and 1·71 at 860°. The theoretical value for complete dissociation is 1·69. As in the case of ammonium chloride, the vapour in H. St. C. Deville and L. Troost's experiment was not completely sat. with ammonium bromide, and the system was not in equilibrium. A. Smith and R. P. Calvert find the **dissociation pressure** of ammonium bromide to be 760·0 mm. at 294·6°, and that the observed results can be represented by $\log p=-2056·541/T+9·54014 \log T-20·98468$. A. Smith and R. H. Lombard find the sat. vapour densities in grms. per c.c.; the percentage degrees of dissociation; the averaged **dissociation constants,** K; and the **latent heat of vaporization** of ammonium bromide from

$$L=\frac{TP}{760}\left(\frac{2057}{0·4343T^2}+\frac{9·540}{T}\right)\frac{0·02419}{D}\text{ Cals.}$$

to be

	300°	320°	340°	360°	380°	388°
Dissoc. press.	55·0	100·5	178·8	310·4	525·5	644·4
Vap. density	0·000130	0·000192	0·000348	0·000633	0·00110	0·00142
Degree dissoc.	16·1	38·7	31·6	21·7	15·3	8·0
Dissoc. const. K	0·000458	0·000497	0·000483	0·000400	0·000236	0·000158
Latent heat	23·5	28·7	27·4	26·1	24·7	24·1

Consequently, the dissociation constant, K, increases to a maximum at 320°, and then decreases. From J. H. van't Hoff's equation, $d \log K/dT = -Q/RT^2$, this means that the term on the right is negative, and therefore Q, the heat of dissociation, must be positive above 320°, and dissociation will be accompanied by an evolution of heat. The heat of dissociation $Q=A_0-CT^2$, and $d \log K/dT=-A_0/RT^2+C/RT^2+C/R$, does not apply over the range where a change in the sign of Q occurs. With hydrogen iodide, the heat of dissociation: $2HI \rightleftharpoons I_2+H_2$, is exothermal below and endothermal above 320°; with ammonium bromide the heat of dissociation: $NH_4Br \rightleftharpoons HBr+NH_3$, is endothermal below and exothermal above 320°. H. Rassow gave 541·9° for the **melting point** of ammonium bromide, and of mixtures of this salt with potassium bromide. G. Bartha gave 235° for the **boiling point** in vacuo.

The **heat of formation** of ammonium bromide from its elements, bromine liquid, is 81·7 Cals. according to J. Ogier;[5] 65·36 according to J. Thomsen; and 71·2 Cals., bromine gaseous, according to M. Berthelot. J. Thomsen found the heat of the reaction: $NH_3+HBr=NH_4Br+45·03$ Cals., and J. M. Eder found the soln. of 25 grms. of the salt in 50 grms. of water lowers the temp. 16°; and J. Thomsen (1877) gives the **heat of solution** of a mol. of the salt in 200 mols. of water −4·4 Cals. J. H. Long gives −4·38 Cals. S. Arrhenius found **the heat of neutralization** in dil. aq. soln. is 12·4 Cals., the **specific heat** of a 2·6 per cent. soln. 0·968 at 18°.

The **solubility** of ammonium bromide in water has been measured by J. M. Eder,[6] and by A. Smith and H. E. Eastlack—the values of the latter are, in grms. of salt per 100 grms. of water:

	0°	10°	20°	30°	40°	60°	80°	100°
NH_4Br	60·6	68·0	75·5	83·2	91·1	107·8	126·0	145·6

The solubilities were carried up to 170° in a sealed tube, and there is a well-defined break in the curve at 137·3°. F. E. C. Scheffer's equations for the solubility curves have been indicated above. The **specific gravity**[7] at 15° is 1·0326 for 5 per cent. soln.; 1·0652, 10 per cent.; 1·1285, 20 per cent.; 1·1921, 30 per cent.; and 1·2920 for 41·09 per cent. soln. A. Smith and H. E. Eastlack found the sp. gr. of sat. soln. to be 1·29 at 15°; 1·66 at 113°; 1·71 at 137°; and 1·76 at 158°. W. W. J. Nicol, and W. H. Perkin give the interpolation formula for soln. at 20°—water unity at 4°—containing w per cent. of salt, $D=1+0·00506w+0·000045w^2$. Soln. of ammonium bromide occupy a greater volume than the sum of the components.[8] For example, the observed sp. gr. D_1, the sp. gr. D computed from $D_0=100/\{(p_1/D_1)+(p_2/D_2)\}$, where p_1 and p_2 respectively denote the percentage amount of salt and water in the soln., and D_1 and D_2 the corresponding sp. gr. of salt and water.

TABLE XXVIII.

Per cent. of NH_4Br.	D	D_0	Volume of 100 grms. of soln.	Volume of Components.	Expansion. Observed.	Expansion. Per cent.
10·81	1·06265	1·0669	88·6687	87·7401	0·9286	1·058
15·31	1·09048	1·0973	86·5351	85·5590	0·9761	1·141
21·28	1·12976	1·1408	78·2290	76·5650	1·6640	2·173

The data, of which the numbers in the last column are but an abstract, lie on a straight line, showing that the expansion of soln. of ammonium bromide is proportional to the conc.; and smaller than with soln. of ammonium chloride. According to W. Ostwald, if *m* grams of the salt be dissolved in 2000-*m* grams of water at 20°, the volume of the fluid increases 47·0 c.c. per mol. (98 grms.). J. Traube calculates the mol. vol. of ammonium bromide in soln. to be 44·3 and 44·8, for 25·0 and 40·428 per cent. soln. when the value for the solid salt is 41·0.

The relative mol. **compressibility** of ammonium bromide in 700 mols. of solvent is 0·973, and in 1500 mols. of the solvent, 0·951—*vide* ammonium iodide. W. C. Röntgen and J. Schneider[9] also measured the **surface tension** of these soln. The **viscosity** of ammonium bromide at 25° decreases from 0·008867 dynes per sq. cm. for 0·216*N*-soln. to 0·008254 for 2·646*N*-soln., and then increases from this minimum to 0·008560 with 4·920*N*-soln. The respective sp. gr. of these soln. are 1·0121, 1·1414, and 1·2605. The values for 1·63*N*-soln. decrease from 0·0116 at 10°, to 0·0077 at 30°, to 0·0056 at 50°. The **velocity of diffusion** of ammonium bromide in aq. soln. is smaller than that of potassium bromide, and greater than sodium bromide.[10]

G. Tammann[11] found the **vapour pressure** of water is lowered by the soln. of ammonium bromide 2·6 mm. for 14·5 grms. of salt per 700 grms. of water; 12·8 mm. for 60·82 grms. of the salt. L. C. de Coppet found the temp. of maximum density of water is lowered 8·7° per mol. per litre.

O. Reinkober studied the reflexion spectra for **ultra-red rays.** According to J. H. Gladstone and W. H. Perkin,[12] the **molecular refraction, dispersion,** and **magnetic rotation** of the ammonium halides are:

	Mol. refraction.	Mol. dispersion.	Mol. magnetic rotation.
NH_4Cl . . .	22·33	1·52	6·096
NH_4Br . . .	28·53	2·49	10·177
NH_4I . . .	39·66	4·88	19·996

The **electrical conductivity** λ of soln. of ammonium bromide[13] at 25° for soln. with a mol. of the salt in *v* litres of water, is:

v . .	2	8	16	32	128	512	1024
λ . .	115·1	123·6	127·4	131·7	137·9	141·3	140·9
a . .	81·7	87·7	90·4	93·5	97·9	100·0	100·0

The percentage degrees of ionization a are computed by H. C. Jones and A. P. West. The results agree with S. M. Johnston's determinations of the raising of the b.p. for *N*-soln., but for higher conc. there are indications of hydrolysis. At ordinary temp. the amount of hydrolysis is imperceptible, but at higher temp. the hydrolysis is more marked, for example, at the b.p. ammonia gas is given off. A. Naumann and A. Rücker found the degree of hydrolysis of a 2*N*-soln. to be 0·03 per cent. at the b.p. J. M. Eder[14] found that when a current of air is passed through the aq. soln. at 30°, ammonia is given off, and the residual liquid contains free hydrobromic acid. M. le Blanc found the **decomposition potential** of a normal soln. with platinum electrodes to be 1·4 volt, about 0·2 volt smaller than with the corresponding compound of potassium or sodium. The **transport number** for the $K^{\cdot}$- and NH_4-ions is almost the same. O. Gropp measured the electrical conductivity of a liquid and frozen soln. of ammonium bromide.

Ammonium bromide dissolves in various organic solvents. *Ethyl alcohol* at 15° dissolves 2·97 per cent. of the salt; at 19°, 3·12 per cent.; and at 78°, 9·50 per cent. *Methyl alcohol* at 19° dissolves 11·1 per cent.; and *ether* (sp. gr. 0·729) dissolves 0·123 grm. of salt per 100 grms. of solvent. G. Tammann and W. Hirschberg have measured the sp. gr. of alcoholic soln.; and measurements on the lowering of the f.p. and the electrical conductivities by G. Carrara and by H. C. Jones and C. L. Lindsay show that the salt is considerably ionized in these soln.—*vide* alkali bromides. Similar remarks apply to soln. of ammonium bromide in *acetone* by P. Dutoit and A. Levier, and in *formic acid* by H. Zanninovich-Tessarin. In the

latter case, the lowering of the f.p., but not the electrical conductivity, shows that the ionization increases to a maximum and then decreases with increasing dilution —*e.g.* with 1·769*N*-, 2·629*N*-, and 2·893*N*-soln., the degrees of ionization by the f.p. method are respectively 55, 86, and 73 per cent. The electrical conductivity of soln. of ammonium bromide in *liquid ammonia* have been determined by H. P. Cady,[15] and by E. C. Franklin and C. A. Kraus, and the results show (i) that although the mol. conductivities are greater than with aq. soln., the degree of ionization is less because the mobility of the ions is very large; and (ii) the eq. conductivity falls from 103·8 at $-32°$ to 2·93 at 133°. The initial increase is ascribed to the increased mobility of the ions which is always augmented as the temp. rises; again, as the solvent approaches its critical state, the ionization decreases, and the decrease from the one cause overpowers the increase from the other cause when the temp. exceeds 10°.

Ammonia was found by L. Troost [16] to unite with ammonium bromide, forming a series of ammino-compounds which are analogous with the corresponding ammino-compounds of ammonium chloride; and they are formed in the same manner. **Ammonium ammino-bromide,** $HBr.2NH_3$, is formed when pulverulent ammonium bromide is exposed to ammonia gas below 5°. The vapour tension is 90 mm. at $-27°$; 350 mm. at 0°; 775 mm. at 14·8°; and 1660 mm. at 31°. The absorption of ammonia may continue until a liquid **ammonium triammino-bromide,** $H_4NBr.3NH_3$, or $HBr.4NH_3$, which when rapidly cooled to about $-20°$, forms a mass of rhombohedral plates which melt at 6° (L. Troost), or 8·7° (H. W. B. Roozeboom). The dissociation press. $NH_4Br.3NH_3 \rightleftharpoons NH_4Br.NH_3+2NH_3$ is 162 mm. at $-21°$; 577 mm. at 0°; 770 mm. at 5°; and 815 at 6·5°. The curve *AB*, Fig. 31, represents the dissociation press. of $NH_4Br.3NH_3$; at *B*, there are two possibilities, for the compound may form the monammino-compound, $NH_4Br.NH_3$, curve *BE*, and a liquid whose empirical composition may be represented by $NH_4Br.nNH_3$, where *x* decreases continuously with rise of temp. until it becomes unity, at the m.p. of the monammino-compound. The curve *EB* may also pass into the metastable region *BD*. At *B* (6·5°, and 815 mm.) the two solid phases, $NH_4Br.NH_3$ and $NH_4Br.3NH_3$, the liquid phase, $NH_4Br+2·63NH_3$, and gaseous NH_3, are in equilibrium. The second possibility is represented by the curve *BC*, which represents a system with solid ammonium triammino-bromide, and a liquid phase $NH_4Br.nNH_3$, where *n* increases with a rise of temp. until liquid and solid have the same composition, and this state is represented by the point C (8·7° and 1140 mm.), the m.p. of the triammino-compound. The curve *CG* represents a mixture of the tri- and a higher ammino-compound. The curve *BZ* represents the equilibrium condition between the two solid phases and a soln. of $NH_4Br+nNH_3$. J. Kendall and J. G. Davidson studied the f.p. curve of mixtures of ammonia and ammonium bromide; they isolated the triammino-salt with an m.p. 13·7°, but obtained no evidence of an hexammino-salt. L. Troost prepared crystals of **ammonium hexammino-bromide,** $NH_4Br.6NH_3$, or $HBr.7NH_3$, which freezes at $-45°$, and melts at $-20°$. The dissociation press. at $-32°$ is 540 mm.; at $-25·3°$, 700 mm.; at $-21·8°$, 835 mm.; and at $-2·8°$, 1745 mm.

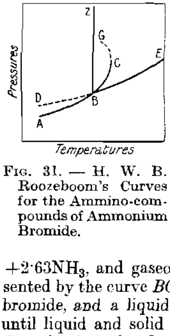

FIG. 31. — H. W. B. Roozeboom's Curves for the Ammino-compounds of Ammonium Bromide.

According to M. Berthelot,[17] ammonium bromide unites with hydrogen bromide, forming a compound—possibly **ammonium hydrodibromide,** $NH_4Br.HBr$—which in contact with mercury gives off hydrogen. Much heat is evolved when a soln. of 9·8 grms. of ammonium bromide in 13·93 grms. of water is treated with 8·39 grms. of bromine; and on evaporation of the soln., over conc. sulphuric acid, rhombic or monoclinic crystals with the colour of potassium dichromate are formed. These crystals have a composition corresponding with **ammonium tribromide,** NH_4Br_3. The compound is formed during the electrolysis of a conc. soln. of ammonium bromide

—there is no risk of forming nitrogen bromide analogous to the explosive nitrogen chloride formed when a soln. of ammonium chloride is treated in the same manner. Ammonium tribromide at ordinary temp. loses bromine: $NH_4Br_3 = NH_4Br + Br_2$ when exposed to the air for one or two hours; and the loss is rapid at 50°. F. Ephraim gives for the dissociation press., 20 mm. at 17°; 159 mm. at 60·4°; 175 mm. at 84·2°; and 670 mm. at 92·3°. Ammonium tribromide is easily soluble in water, and the soln. smells strongly of bromine. The bromine can be removed from the soln. by a stream of air, by extraction with chloroform, or carbon disulphide. H. W. B. Roozeboom[18] also found evidence of the formation of a higher polybromide—possibly **ammonium pentabromide,** NH_4Br_5—from the heat developed by the action of bromine on the tribromide, but the compound was not isolated. C. L. Jackson and I. H. Derby reported that ferrous hexammino-iodide, $FeI_2.6NH_3$, absorbed large quantities of bromine to form a reddish-brown powder soluble in ether. When the ethereal soln. is evaporated, **ammonium bromoiodide,** NH_4IBr_2, remains as a lustrous green powder—blood-red in transmitted light, and green in reflected light. The same compound is formed by the action of an ethereal soln. of iodine bromide on ammonium bromide. It readily decomposes on exposure to the air, forming, it is said, ammonium bromide. F. Ephraim found the dissociation press. of NH_4IBr_2 to be 65 mm. at 107°; 204 mm. at 134°; 465 mm. at 165·4°; and 40 mm. at 161°. Similarly for **ammonium chlorodibromide,** NH_4ClBr_2, the dissociation press. is 70 mm. at 18·5°; 310 mm. at 41·5°; 608 mm. at 54°; and 680 mm. at 55·8°.

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§ 19. The Alkali Iodides

The history of the iodides dates from the time of J. L. Gay Lussac's discovery [1] of hydriodic acid in 1813. Iodides occur in sea-water, and in the waters of many natural springs and brines. Iodides also occur in varec; in the nitre beds of South America; and in many natural phosphates. In whatever form iodine occurs in these substances, it is usual to extract this element as iodine, and subsequently to convert this into the iodide—generally potassium iodide. Potassium iodide is used in analytical and photographical work, and medicinally for the treatment of scrofulous, rheumatic, and syphilitic diseases. Sodium iodide is used as a precipitant for gold and silver in the treatment of weak copper ores from Tharsis, etc.

The preparation of the alkali iodides.—V. Merz and W. Weith [2] found that metallic sodium may be melted with iodine without any marked interaction even at 350°–360° there is but a superficial change. Similar results were obtained with bromine. Potassium, however, unites with iodine under the influence of a slight press., and with iodine vapour union is attended by the evolution of heat and light. Iodine vapour also drives some oxygen from red-hot potassium hydroxide.

The alkali iodides were first made by J. L. Gay Lussac,[3] in 1813, by the action of an aq. soln. of hydriodic acid on potassium hydroxide, or carbonate, and the conc. of the soln. to the crystallizing point by evaporation. The process with hydriodic acid is expensive, but it is the most direct, and it gives a pure product. It is therefore preferred for the rarer alkali iodides.

The alkali iodides can also be made by dissolving iodine in the alkali hydroxide to form a mixture of iodide and iodate: $6KOH+3I_2=5KI+KIO_3+3H_2O$. The soln. is evaporated to dryness, and calcined in glass, porcelain, fireclay, or cast-iron vessels up to the point at which oxygen ceases to be evolved.[4] The residue is leached with water, and the soln. evaporated to the crystallization temp. If large masses of soln. are evaporated slowly, very fine crystals are produced. The crystals are dried on hot plates in a current of air. There is a slight loss of iodine by decrepitation and volatilization during the evaporation and calcination. The reduction of the iodate is facilitated by mixing powdered charcoal [5] with the conc. soln., and after the evaporation to dryness, and calcination, extracting the mass with water, and proceeding with the soln. as before. The preparation of iodide by the potash process is recommended by the British Pharmacopœia. The potash-lye

ought to have a high purity since most of the impurities in commercial potassium hydroxide remain with the iodide and are not separated by recrystallization. A start is therefore made from commercial but highly purified potassium carbonate; this is causticized with lime, and then treated with iodine. C. F. Mohr recommended sugar or starch in place of charcoal, and also suggested the use of ferrous iodide for reducing the iodate. E. Turner reduced the iodate with hydrogen sulphide and filtered off the dissolved sulphur. R. Schindler condemns E. Turner's recommendation, for he says that some iodine is lost with the sulphur, and the final product is contaminated with sulphur. P. Chappe and O. Malissi recommended reducing the iodate with iron filings; and J. N. von Fuchs heated an intimate mixture of iodine (100), water (240), potassium carbonate (75), and iron (30) until the evolution of carbon dioxide had ceased. The dried product was calcined at a dull red-heat, and the iodide extracted with water.

The iodine can be first converted into a metal iodide and the product treated with a potassium salt—*e.g.* potassium carbonate, sulphate, or hydroxide—to precipitate the heavy metal. The soln. of potassium iodide so formed is then evaporated in the usual way. J. von Liebig[6] converted the iodine into barium iodide by adding baryta water to a warm soln. made by adding iodine to warm water in which red phosphorus is suspended. Barium phosphate precipitates, and a soln. of barium iodide is formed. J. R. Wagner added iodine to a slip made of barium sulphite and hydroxide. J. von Liebig, and M. Pettenkofer used lime in place of baryta. A. le Royer and J. B. A. Dumas made zinc iodide by the joint action of iodine, water, and zinc; and precipitated the zinc as carbonate by potassium carbonate. C. Langbein treated the iodiferous mother liquors from the Chili saltpetre works with a copper salt, and after washing the precipitated cuprous iodide, treated the cuprous iodide suspended in water with hydrogen sulphide. The resulting hydriodic acid was neutralized with potassium carbonate, and evaporated for crystallization. Any sulphur which separates during the evaporation is removed. G. S. Sérullas prepared antimony iodide by heating an intimate mixture of the two elements. The powdered iodide was decomposed by hot water whereby a soln. of hydriodic acid and a precipitate of antimony oxyiodide was formed. The clear liquor was neutralized with potassium carbonate, and the soln. of potassium iodide evaporated to crystallization. A. Cailliot, S. Baup, J. von Liebig, and others prepared ferrous iodide by the joint action of iodine, iron, and water, and decomposed the product by treatment with potassium carbonate. This is the principle of the present-day process for the manufacture of this salt, and the process is illustrated by the following method of preparation:

Shake about 8 grms. of iron filings with 50 c.c. of water in a small flask and gradually add 25 grms. of iodine in small quantities at a time while keeping the mixture cool. The mixture is then warmed, and when all the iodine has reacted with the iron the soln. of ferrous iodide has a deep yellow colour. Decant the liquid from the excess of iron, wash with a little water, and add 5 grms. more of iodine so as to oxidize the ferrous salt and subsequently furnish a precipitate which filters easily. Warm the soln. until all the iodine is dissolved, and pour the mixture of ferrous and ferric iodide into a boiling soln. of 17 grms. of potassium carbonate in 50 c.c. of water. Carbon dioxide is copiously evolved, and a mixture of ferric and ferrous hydroxides is formed which makes the mixture very thick, but on further heating the precipitate coagulates. If a little of the filtered soln. is not colourless, more potassium carbonate is required. Evaporate the filtrate until crystallization begins, and allow the soln. subsequently to evaporate slowly by placing it in a warm place. Drain the crystals in a funnel, wash with a very little cold water, and the mother liquid may be further evaporated for another crop of crystals. In all, from 25 to 35 grms. of potassium iodide can be so obtained.

J. von Liebig's modification avoids the slow soln. of iodine, and the troublesome frothing by the escape of carbon dioxide in the later stages of the reaction. A soln. of 1·2 parts of iodine, 3 of iron, and 32 of water is mixed with a soln. of 6 parts of iodine in 12 parts of potash-lye of sp. gr. 1·345, and finally with 9 parts of the same liquid. The mixture is boiled, filtered, and evaporated to dryness. The

soluble iodide is leached from the insoluble ferric oxide, and crystallized. The product is free from iodate, and the yield is good. O. Hesse converted the iron iodide into calcium iodide by treatment with milk of lime, and then treated the boiling soln. with potassium sulphate, and allowed the mixture to stand for six hours. The clear liquid was evaporated to crystallization.

G. Taddei[7] prepared potassium iodide by adding a dil. soln. of potassium monosulphide to an alcoholic soln. of iodine. In place of potassium sulphide, J. von Liebig and C. Wittstock used barium sulphide, prepared by calcining sulphate with coke. According to R. Schindler, the products obtained by the sulphide process are contaminated with sulphur compounds. G. S. Sérullas treated potassium antimoniate (prepared by calcining tartar emetic) with an alcoholic soln. of iodine as long as the soln. was decolorized. The filtered soln. was evaporated to the point of crystallization.

Potassium iodide can also be obtained from the aq. extract of kelp or from the mother liquid remaining after the separation of sodium chloride and potassium sulphate from sea-water by evaporation. In E. Allary and J. Pellieux' process,[8] the liquid is evaporated to dryness and roasted in a special furnace so as to avoid a loss of iodine. The product is fractionally extracted with cold water, when a soln. is obtained which on evaporation gives a residue with 50 per cent. of alkali iodide. This product is extracted in a special digester with 50 per cent. alcohol. The solvent dissolves little more than the iodides. The alcohol is distilled off, and on evaporation a residue containing about 34 per cent. of potassium iodide, and 66 per cent. of sodium iodide is obtained. To convert the latter into potassium iodide, the proper quantity of a soln. of potassium carbonate is added and carbon dioxide passed into the liquid whereby sodium bicarbonate is precipitated. The precipitate is separated by a filter press, and the small amount of sodium bicarbonate remaining in the soln. is separated by the addition of a little hydrochloric acid and the sodium chloride and potassium iodide separated by fractional crystallization. In E. Sonstadt's process, the mother liquid is treated with chlorine mixed with potassium chlorate or permanganate so as to convert the iodine into iodate. A soln. of a barium salt is added, and the barium iodate treated with potassium sulphate. Barium sulphate is precipitated, and the soln. of potassium iodate is evaporated to dryness and calcined to convert the iodate to iodide. The latter is purified by crystallization.

The impurities of potassium iodide.—The potassium iodide used for medical purposes should contain no iodate since this salt is poisonous; it should not therefore be compounded with anything liable to form an iodate—*e.g.* potassium chlorate. J. Lepage recommended purifying potassium iodide by digesting 4 grms. with 55 grms. of 92 per cent. alcohol, and after standing 24 hrs. most of the impurities will remain undissolved. Most of the likely impurities are easily detected. The presence of *iodate* is detected by adding tartaric acid which liberates hydriodic acid from the iodide and this reacts with iodate liberating iodine. The addition of a little starch paste with the tartaric acid shows up the iodine as blue starch iodide.[9] H. N. Morse and W. M. Burton removed iodates by boiling a soln. of the iodide with zinc amalgam prepared by agitating zinc dust with mercury in the presence of tartaric acid, and subsequently washing with water. The filtrate is free from zinc, mercury, and iodates. E. Schering has reported the presence of *lead in commercial potassium iodide*. C. Daudt reported *sulphites*; and F. A. Flückiger *cyanides* derived from the cyanogen impurity of iodine. R. Schindler found sulpho-organic substances, derived possibly from the use of alcohol and hydrogen sulphide in some obsolete processes of preparation. Potassium iodide should not lose weight on drying owing to the loss of *water*. The presence of *sulphates* is shown by the soln. giving a precipitate insoluble in nitric acid when treated with barium chloride. The presence of a trace of *carbonate* is shown by a cloudiness or turbidity with lime or baryta water, soluble in nitric acid. If an appreciable quantity of carbonate be present, the salt will have an alkaline reaction, it will be deliquescent,

and it will not dissolve in six parts of cold alcohol of sp. gr. 0·85. According to C. Meinecke, carbonates can be removed by shaking the soln. with zinc iodide, and filtering from the precipitated zinc oxide. The presence of *chlorides* is shown by precipitation with silver nitrate, and agitation with ammonia. The ammoniacal soln. should give no precipitate with nitric acid. The potassium iodide of commerce nearly always contains some sodium or potassium chloride—a good commercial sample is reported with 0·2 per cent. of potassium chloride, 99·5 of potassium iodide, and the remainder water.

The properties of the alkali iodides.—The alkali iodides all crystallize in well-defined cubic **crystals** frequently *en trémies*. According to R. Warrington,[10] when deposited from alcoholic soln., potassium iodide is deposited in long needle-like crystals; opaque crystals are obtained if deposited from hot soln., or from soln. containing potassium carbonate. J. W. Retgers found that cubic crystals are obtained with soln. containing a little urea; chromic or ferric chloride; or lead chloride. H. Schwendenwein discussed the **space lattice** of the alkali iodides. K. Fajans and K. F. Herzfeld estimated the distances apart of the atoms in the space lattices of sodium, potassium, and rubidium iodides to be respectively $3·231\times10^{-8}$, $3·527\times10^{-8}$, and $3·672\times10^{-8}$ cm., and the respective lattice energies to be 146·7, 139·1, and 135·8 Cals. per mol. E. Newbery and H. Lupton [11] found that potassium iodide is coloured brown by exposure to radium emanation, but no trace of free iodine can be detected when the crystal is dissolved in water. The crystals glow with a bluish light during the exposure. M. Trautz [12] obtained a glow of light on precipitating hot sodium or potassinm alcoholate with hydriodic acid; but he says it is not due to **crystalloluminescence** but rather to the action of alcohol on iodine. E. F. Farnau obtained a faint glow on precipitating potassium iodide with alcohol, and H. B. Weiser verified this observation and obtained good results at 25° by precipitation with hydriodic acid of sp. gr. 1·595. E. F. Farnau claimed to have obtained crystalloluminescence with sodium iodide, but H. B. Weiser obtained negative results.

The **specific gravity** of lithium iodide is 3·485 (23°), according to F. W. Clarke.[13] For sodium iodide, P. A. Favre and C. A. Valson give the sp. gr. 3·654. The older determinations of the sp. gr. of potassium iodide, range from the 2·850 of H. Schiff to C. J.B. Karsten's, 2·908; H. Buignet's, 2·970; J. Y. Buchanan's, 3·043 (23·4°); E. Filhol's, 3·056; L. Playfair and J. P. Joule's, 3·048 to 3·070; H. G. F. Schröder's, 3·077 to 3·083; P. F. G. Boullay's, 3·104; W. Spring's (fused), 3·012 (20°), and after subjection to a press. of 20,000 atm., 3·110 (22°), and after a repetition of the compression, 3·112 (20°); B. Gossner gives 3·124; J. A. Craw, 3·091; and M. Sprockhoff, 3·131. G. Quincke gives 3·076 for the sp. gr. of potassium iodide at 0°, and 2·497 at the m.p. For rubidium iodide, C. Setterberg gives 3·567; and M. Sprockhoff, 3·131. G. Quincke gives 3·076 for the sp. gr. of potassium iodide at 0°, and 2·497 at the m.p. For rubidium iodide, C. Setterberg gives 3·567; and M. Sprockhoff, 3·564. For cæsium iodide, C. Setterberg gives 4·537; and M. Sprockhoff, 4·539. G. P. Baxter and C. C. Wallace's data may be regarded as embodying the best representative values for the salts named:

Temp.	LiI	NaI	KI	RbI	CsI
70·19°	4·038	—	—	-	4·480
50·04°	4·048	3·653	3·114	3·542	4·493
25·00°	4·061	3·665	3·123	3·550	4·509
0°	4·074	3·677	3·133	3·560	4·525

Some volume relations, mol. vol., and sp. gr. of the molten halide salts have been indicated previously. J. M. Jäger [14] gives for the sp. gr. D of the molten sodium iodide at $\theta°$ (water at 4° unity), $D=2·698-0·001061(\theta-700)$; potassium iodide, $D=2·431-0·001022(\theta-700)$; rubidium iodide, $D=2·798-0·001107(\theta-700)$; and cæsium iodide, $D=3·175-0·001222(\theta-640)$. K. Fajans and H. Grimm studied the mol. vol. of the alkali iodides. G. Quincke's value for the **capillary constant** of molten potassium iodide is $a^2=4·84$; and the **surface tension,** 59·3 dynes per

c.m. J. M. Jäger gives the values indicated in Table XXIX. for the sp. gr. the surface tension (ergs per cm.), and the mol. surface energy (ergs per sq. cm.) of the molten iodides.

TABLE XXIX.—SPECIFIC GRAVITIES AND SURFACE TENSIONS OF THE ALKALI IODIDES.

	Temp.	Surface tension.	Sp. gr.	Mol. surface energy.	Temp. coeff. per degree.
NaI	705·5°	85·6	2·692	1248·2	0·29
	860·7°	77·6	2·527	1180·4	0·63
KI	737°	75·2	2·392	1269·8	1·58
	873°	66·5	2·225	1169·6	0·67
RbI	673·4°	79·4	2·827	1413·7	0·95
	1016°	55·4	2·448	1085·7	0·95
CsI	653·6°	73·1	3·158	1382·5	0·82
	1030°	51·1	2·699	1073·0	0·82

T. W. Richards and G. Jones' value for the **compressibility** of sodium iodide is $6·9\times10^{-6}$ megabars, and of potassium iodide, $8·6\times10^{-6}$ megabars. For the effect of press. on the sp. gr. of a potassium iodide, *vide* the alkali chlorides.

The **melting point** of anhydrous lithium iodide is 430°, according to W. Ramsay and N. Eumorfopoulos,[15] 446° ± 3·5° according to T. Carnelley, and 440° according to G. Scarpa. The first named also give 663° for the m.p. of sodium iodide; V. Meyer and W. Riddle give 661·4°; N. S. Kurnakoff and S. F. Schemtschuschny give 660°; G. Scarpa gives 665°; H. Brand gives 653°; J. McCrae gives 695°; O. Ruff and W. Plato give 650°; and K. Hüttner and G. Tammann give 650°. For potassium iodide, V. Meyer and W. Riddle give 684·7°; J. McCrae gives 723°; G. Scarpa gives 695°; N. S. Kurnakoff and S. F. Schemtschuschny give 693°; H. Rassow gave 684·1°; O. Ruff and W. Plato give 705°; H. Brand gives 678°; and K. Hüttner and G. Tammann give 680°. For rubidium iodide, V. Meyer and W. Riddle give 641·5°; and T. Carnelley, 642°. For cæsium iodide, V. Meyer and W. Riddle give 621°. Consequently, *the melting point of the alkali halides with any particular halogen decreases with increasing atomic weight of the alkali metal from sodium to cæsium, and the melting point of the lithium salt is less than that of the sodium salt.* Thus, the best representative values from some divergent data are:

	Li	Na	K	Rb	Cs
Chlorides	613°	801°	773°	714°	645°
Bromides	547°	760°	730°	685°	—
Iodides	446°	752°	698°	642°	621°

Hence, also, *the melting point of the halide of any particular alkali metal decreases with increasing atomic weight of the halogen.* G. Scarpa found that the binary system lithium hydroxide and iodide gives a eutectic at 180° with 45 mols. per cent. of the hydroxide; a break at 410° corresponds with the formation of unstable **lithium tetrahydroxyiodide,** 4LiOH.LiI; the system sodium hydroxide and iodide gives a decomposable compound—probably sodium dihydroxy-tri-iodide, 2NaOH.3NaI; the binary system of potassium hydroxide and iodide gives a simple eutectic at 250° with 73 mols. per cent. of KOH. The general results with the alkali hydroxides and the corresponding halides of the same metal show that the tendency to form compounds increases on passing from potassium to lithium, or with the decreasing electro-affinity of the ions. The general results are summarized:

	Fluorides.	Chlorides.	Bromides.	Iodides.
LiOH	*SS*	2LiOH.3LiCl	3LiOH.LiBr	4LiOH.LiI
NaOH	*SS*	*SS*	*V*	2NaOH.3NaI
KOH	*S*	*SS*	*V*	*V*

where *V* denotes a simple eutectic, *S* the formation of mixed crystals in any proportion, and *SS* the formation of mixed crystals with a break. L. H. Borgström

gives 1350° for the **boiling point** of sodium iodide, and 1420° for potassium iodide; and G. Bartha respectively 610° and 570° in the cathode light.

According to R. Schindler,[16] potassium iodide volatilizes in free air when heated to the softening temp. of hard glass, and, according to R. Bunsen, and T. H. Norton and D. M. Roth, it volatilizes from 0·352 to 0·423 times as fast as the same quantity of sodium chloride when heated in the hottest part of a Bunsen's flame. According to J. Dewar and A. Scott,[17] the vapour density of potassium iodide is 169·8. A. von Weinberg obtained 43·3 Cals. for the **heat of sublimation** of sodium iodide, and 44·9 Cals. for that of potassium iodide; and A. Reis obtained for sodium and potassium iodides respectively 51 and 46 Cals., and between 15 and 35 Cals. for lithium iodide.

The **specific heat** of sodium iodide is 0·0881 between 26° and 50° according to J. H. Schüller,[18] and, according to H. V. Regnault, 0·0868 between 16° and 99°; and for potassium iodide, 0·0819. J. N. Brönsted gives for the sp. ht. of the alkali iodides between 0° and 20°:

	NaI	KI	RbI	CsI
Sp. ht.	0·0821	0·0741	0·0581	0·0477
Mol. ht.	12·31	12·30	12·34	12·39

F. Koref obtained for the sp. ht. and mol. ht. of sodium iodide between −191·8° and −81·3°, respectively 0·0740 and 11·10; and between 0° and −76·4°, 0·1170 and 12·04. Similarly for potassium iodide between −191·0° and −80·1°, respectively 0·673 and 11·17; and between 0° and −77·1°, 0·735 and 12·21. A. Bodisco[19] gives the **heat of formation** of lithium iodide from its elements $Li+I_{gas}=LiI_{solid}+68·0$ Cals., 82·8 Cals.; for sodium bromide, 69·08 Cals.; for potassium iodide, 84·1 Cals. (M. Berthelot), 80·13 Cals. (J. Thomsen); and, according to N. N. Beketoff, for cæsium iodide, 86·564 Cals. A. von Weinberg gave 129·0 Cals. for the heat of dissociation of lithium iodide; 120·9 Cals. for that of sodium iodide; 126·6 Cals. for potassium iodide; 127·9 Cals. for rubidium iodide; and 129·8 Cals. for cæsium iodide. The **heat of neutralization,** $NaOH_{aq}+HI_{aq}=13·68$ Cals.; $KOH_{aq}+HI_{aq}=13·58$ Cals. The **heat of solution** of lithium iodide is 14·8 Cals.; sodium iodide, 1·30 Cal. (M. Berthelot), 1·22 Cal. (J. Thomsen); potassium iodide, −5·11 Cals. (J. Thomsen), −5·32 Cals. (M. Berthelot), and M. Berthelot and L. Ilosvay de Nagy Ilosva give for the heat of soln. of a mol. of potassium iodide in 200 mols. of water at a temp. θ as $-5·18+36(\theta-15)$ Cals. The heat of soln. of cæsium iodide is −8·164 Cals., according to N. N. Beketoff. The **heat of hydration:** $NaI+2H_2O=NaI.2H_2O+5·23$ to 5·30 Cals.

The alkali iodides are very soluble in water; the **solubilities** of lithinm, sodium, and potassium iodides in 100 grms. of water are as follows:

	0°	10°	20°	40°	60°	80°	100°
LiI	151	157	165	171	202	263 (75°)	—
NaI	158·7	168·6	178·7	205	256·8	296 (80°)	302
KI	127·5	136	144	160	176	192 (80°)	208

The values for lithium iodide are by P. Kremers; the others are by P. Kremers (1856), A. Étard, and L. C. de Coppet.[20] The solid phase for sodium iodide from 148 at −20° to 293 at 65° is the dihydrated salts; above this temp. anhydrous sodium iodide is the solid phase, at 120° the solubility is 310, and at 140°, 321. L. C. de Coppet gives the interpolation formula for the solubility S of sodium iodide, from 65° to 140°, in 100 grms. of water: $S=264·19+0·3978\theta$; and A. Étard for 0° to 80°, per 100 grms. of soln. $S=61·3+0·1712\theta$, and from 80° to 160°, $S=75+0·0258\theta$. The values for potassium iodide are by L. C. de Coppet, A. Étard, W. A. Tilden and W. A. Shenstone, F. A. H. Schreinemaker, and A. Meusser. The solid phase with potassium iodide is the anhydrous salt, at −10° the solubility is 115·1; at −5°, 119·8; at 110°, 215; and at 120°, 223. L. C. de Coppet gives the interpolation formula for the solubility S of potassium iodide at $\theta°$ from −22° to 120°, per 100 grms. of water: $S=126·23+0·8088\theta$; and A. Étard from 0° to

165°, per 100 grms. of soln. : $S=55{\cdot}8+0{\cdot}122\theta$. According to T. Reissig, 100 grms. of water at 6·9° dissolve 137·5 grms. of rubidium iodide, and at 17·4°, 152·0 grms. H. W. Foote gives the solubility of cæsium iodide at —4° as 27·68 per cent., at 35·6°, 51·48 per cent. ; and N. N. Beketoff says 100 parts of water at 0° dissolve 44 parts of cæsium iodide ; at 14°, 56·3 parts ; and at 61°, 160 parts. Lithium iodide forms at least three hydrates.[21] At temp. below 75°, **trihydrated lithium iodide,** $LiI.3H_2O$, appears to be the stable form. This hydrate forms deliquescent needle-like crystals which L. Troost supposes to be monoclinic crystals. This hydrate melts at 72° or 73°. It is not altered over sulphuric acid at 0° ; and it crystallizes unchanged from hydriodic acid or from alcohol. It loses water at 120°, and boils at 200°. The transformation points have not been precisely determined, the trihydrated salt melts at 73° without losing water, and near this temp. it passes into **dihydrated lithium iodide,** $LiI.2H_2O$; and this at about 80° forms **monohydrated lithium iodide,** $LiI.H_2O$, which, at about 300°, forms the anhydrous salt. Consequently, with these approximations, the transition points of the hydrated lithium halides are :

			$2H_2O$	H_2O		
$LiCl.3H_2O$	→	−15°	21·5°	98°	→	LiCl
$LiBr.3H_2O$	→	3·5°	44°	159°	→	LiBr
$LiI.3H_2O$	→	75°	80°	300°	→	LiI

The hydrates of sodium iodide [22] resemble those of sodium bromide. **Dihydrated sodium iodide,** $NaI.2H_2O$, is stable over the range —13·5° to 65° ; at the latter

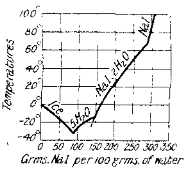

FIG. 32. — Equilibrium Curves of Sodium Iodide and Water.

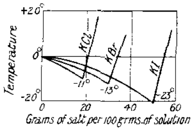

FIG. 33.—Solubility Curves of the Potassium Halides.

temp., the dihydrated salt and anhydrous sodium iodide are stable ; and the former temp. is a transition point between pentahydrated sodium iodide, $NaI.5H_2O$, and the dihydrated salt. These facts are summarized in Fig. 32. According to W. Meyerhoffer, the eutectic temp. between the pentahydrated salt and ice is —31·5°. Potassium iodide forms no hydrates, and, according to F. Guthrie,[23] the eutectic temp. is —22° with soln. of 108·5 grms. of iodide in 100 grms. of water ; R. Kremann and F. Kerschbaum give —23·1° with 109·2 grms. of the iodide in 100 grms. of water. The eutectic temp. are respectively —11°, —13°, and —23°. H. W. Foote's value for the eutectic with ice and cæsium iodide is —4°, with 38·3 grms. of CsI in 100 grms. of water. The solubility curves of potassium chloride, bromide, and iodide in water are shown in Fig. 33. R. Ahegg and A. Hamburger give for the solubilities of the alkali iodides at room temp. :

LiI	NaI	KI	RbI	CsI
12·0	11·5	8·4	7·1	2·7

mols. per litre.

The **specific gravities** of soln. containing n grms. of the alkali halide per 100 grms. :

N	5	10	20	30	40	50	60
LiI (19·5°) .	1·038	1·079	1·172	1·280	1·414	1·575	1·777
NaI (15°) .	1·040	1·082	1·179	1·294	1·432	1·600	1·810
KI (19·5°) .	1·038	1·078	1·066	1·271	1·396	1·546	1·734

A soln. of lithium iodide sat. at 20° has a sp. gr. 1·8. The values for lithium, sodium, and potassium iodides are by P. Kremers and G. T. Gerlach.[24] F. Kohlrausch has also measured the values for the sodium salt; and H. Schiff for the potassium salt at 21°. P. Kremers has calculated the volume changes which occur in these soln. between 0° and 100°. G. P. Baxter has measured the sp. gr. of soln. of the five alkali iodides, and compared the observed mol. vol. of the solids with those computed from the at. vol. of the elements, and with the mol. vol. of the salts in soln.

C. Forch's values for the **coefficient of thermal expansion** of aq. soln. of potassium iodide per litre, are for soln. with 83 grms. of salt per litre: 0·000083 (0°–5°); 0·000146 (5°–10°); and 0·000400 (35°–40°); for soln. with 166 grms. of salt per litre, the numbers are: 0·000173 (0°–5°); 0·000221 (5°–10°); and 0·000427 (25°–40°); and for soln. with 332 grms. per litre, the numbers are: 0·000298 (0°–5°); 0·000323 (5°–10°); and 0·000471 (35°–40°). T. Reissig says that the sp. gr. of a soln. of 0·1 grm. of rubidium iodide per c.c. is 1·0755; and 0·05 grm. per c.c., 1·0353; and H. Erdmann gives the sp. gr. of a cold sat. soln. as 1·726. N. N. Beketoff says the sp. gr. of a sat. soln. of cæsium iodide at 14° is 1·393. The coeff. of linear expansion of crystals of potassium iodide, by H. Fizeau, is $a=0·000042653$ at 40°. The coeff. of cubical expansion of crystals of the alkali halides, determined by G. P. Baxter and C. C. Wallace:

	NaI	KI	RbI	CsI
0° to 25° . .	0·000135	0·000122	0·000112	0·000146
25° to 50° . .	0·000136	0·000114	0·000092	0·000146

The **coefficients of diffusion** of 0·6, 1·9, and 5·4*N*-soln. of potassium iodide at 10° is, according to J. Schuhmeister, respectively 1·12, 1·25, and 1·45 per sq. cm. per day.[25] S. Arrhenius' value for the **viscosity** of soln. of potassium iodide is 0·912 at 17·6°—a value less than for water. F. Körber has measured the effect of press. on the viscosities of soln. of the alkali bromides as indicated in Table XIV. P. B. Davis has discussed the phenomenal lowering of the viscosity of soln. of rubidium and cæsium iodides in glycerol. T. W. Richards and G. Jones [26] found the **compressibility** coeff. of solid sodium iodide at 20° between 100 and 500 atm., to be $7·0\times10^{-6}$ megabars, and of potassium iodide, $8·7\times10^{-6}$ megabars. W. C. Röntgen and J. Schneider measured the compressibility of soln. of lithium and potassium iodides; M. Schumann of sodium iodide; and H. Gibault, and P. G. Tait, of potassium iodide—*vide* ammonium iodide.

According to P. Kremers, the **boiling point** of a sat. soln. of sodium iodide is 121°, and G. T. Gerlach [27] found that a soln. of potassium iodide with 30 grms. of potassium iodide per 100 grms. of water boiled at 102°, with 134 grms. of potassium iodide at 110°; and with 220 grms. of this salt, at 118·5°, and G. J. Mulder found a sat. soln. with 222·6 grms. of salt in 100 grms. of water boiled at 118·4°. The mol. raising of the b.p. of aq. soln. containing 0·199 mol. of sodium iodide per kilogram of water is 0·96°; and with 1·588 mol. of the same salt, 1·102°. The mol. rise in the b.p. increases with increasing conc., while the ionization hypothesis *simpliciter* requires the converse relation. Hence it is inferred that the salt is increasingly hydrated as the conc. of the soln. increases. A. Schlamp [28] found for soln. with 0·260 mol. of potassium iodide per kilogram of water, a mol. rise of 0·98°, and with 6·313 mols., 1·27°. Here again effect of the hydration of the solute is in evidence. According to G. Tammann,[29] the **vapour pressure** of water at 100° is lowered 16·5 mm. by the soln. of 10·05 grms. of sodium iodide in 100 grms. of water, and 244·6 grms. of this salt lower the vap. press. 535·6 mm. Analogous results were obtained at other press. with lithium, sodium, and potassium iodides. At 0°, C. Dieterici found the vap. press. of a soln. with 33·2 grms. of potassium iodide in 100 grms. of water, to be 4·316 mm., and with 124·5 grms. of the salt, 3·474 mm. F. Rüdorff found the f.p. of water containing a gram of the dihydrated sodium iodide per 100 grms. of water is lowered 0·216°; and a gram of potassium

iodide, 0·212. The mol. lowering of the **freezing point** of aq. soln.[30] 0·0759 mols. of lithium iodide in a kilogram of water is 0·275°, and with 0·7480 mols., 3·082°. This resembles the results with lithium chloride and bromide, and is taken as evidence of the hydration of solute or of ions, or both. The mol. lowering of the f.p. of aq. soln. containing 0·0651 mols. of potassium iodide is 3·5°, and with 1·003 mols., 3·37°.

The **specific heat**[31] of soln. of two eq. of sodium iodide in 50, 100, and 200 eq. of water between 20° and 52°, is respectively 0·8092, 0·8864, and 0·9388; and for potassium iodide, 0·7153, 0·8301, and 0·9063 respectively, and for the same salt between 16° and 120°, 0·8760, 0·9280, and 0·9596. J. Thomsen found 0·950 to be the sp. ht. of a soln. of a mol. of potassium iodide in 200 mols. of water at 16°.

The **refractive indices** μ of crystals of potassium, rubidium, and cæsium iodides have been measured by H. Topsöe and C. Christiansen, M. Sprockhoff, and H. Erdmann,[32] and the values for the halides of these three alkali metals may be summarized.

TABLE XXX.—THE REFRACTIVE INDICES OF SOME ALKALI HALIDES.

	C-line.			*D*-line.			*E*-line.		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
Potassium	1·4865	1·5548	1·6593	1·4896	1·5596	1·6674	1·4976	1·5716	1·6880
Rubidium	1·4903	1·5483	1·6397	1·4936	1·5528	1·6474	1·5016	1·5646	1·6672
Cæsium	1·6377	1·6924	1·7784	1·6418	1·6984	1·7876	1·6523	1·7126	1·8118

O. Bender has measured the refractive indices of soln. containing w grms. of sodium and potassium iodide per 100 c.c. of water at 18° for the different spectral lines. For the *D*-line, when w=14·954, $(\mu-\mu_0)/w$=0·001410; and when w=59·816, $(\mu-\mu_0)/w$=0·001377. Similarly, for soln. of potassium iodide, when w=16·562, $(\mu-\mu_0)/w$=0·001272; and when w=49·686, $(\mu-\mu_0)/w$=0·001237. G. P. Baxter has made some careful measurements of the refractive indices of soln. of lithium, sodium, and potassium iodides. M. le Blanc and P. Rohland give the refractive index of potassium iodide 1·6666, the sp. gr. 3·091, and the mol. refraction of the solid, by Gladstone and Dale's formula, is therefore 35·80, and by Lorentz and Lorenz's formula, 19·98. Similarly, 9·35 per cent. soln. with a sp. gr. 1·0726 have the refractive index μ=1·3457; and 11·35 per cent. soln. with a sp. gr. 1·3487, μ=1·3487. The corresponding values by Gladstone and Dale's formula are respectively 36·38 and 36·55; and by Lorentz and Lorenz's formula 21·22 and 21·28 respectively, so that the soln. of the solid in water increases its mol. refraction. B. C. Dannien also measured the refractive index of solid potassium iodide, as well as in aq. and alcoholic soln.

W. Ostwald's values[33] for the **electrical conductivity** λ of soln. of lithium, sodium, and potassium iodides at 25°, and P. Walden's for rubidium iodide at 0°, for a mol. of the salt in v litres of water, are:

v	32	64	128	256	512	1024
LiI	103·8	106·4	111·6	112·0	114·0	114·5
NaI	112·7	116·5	119·7	122·8	125·7	127·0
KI	137·0	140·8	144·3	147·1	148·8	150·0
RbI	74·6	76·5	78·4	80·2	80·6	82·3

F. M. Jäger and B. Kampa measured the mol. conductivity, μ, of potassium iodide at θ between 691·5° and 814° to be $\mu=85·41+0·1564(\theta-700)$. P. Walden studied the relation between the viscosity and conductivity of soln. of potassium and sodium iodides. F. Kohlrausch has also measured the sp. gr. and specific conductivities of soln. of potassium iodide of various conc., and computed the degree of ionization, a.

F. Kohlrausch and H. von Steinwehr find for a 0·0001*N*-soln., a is 99 per cent.; for 0·001*N*-soln., a=97·8; for 0·01*N*-soln., a=94·2; for 0·1*N*-soln., a=86·9; and for 1·0*N*-soln., a=79·1 per cent. The temp. coeff. of the conductivity between 18° and 52° is, according to S. Arrhenius, for 0·001*N*-soln., 0·0231; for 0·01*N*-soln., 0·0225; for 0·1*N*-soln., 0·0221; and for 0·5*N*-soln., 0·0207. For $\frac{1}{10}$*N*-soln. at 35°, S. Arrhenius computes the **heat of ionization** to be −916 cals. The **transport number** for the anions of 0·05*N*-soln. of potassium iodide at 25° is 0·505; W. Hittorf [34] found 0·511 for 0·7*N*- to 2*N*-soln., and 0·492 for 0·035*N*-soln. at 3°. The transport number of potassium iodide has been determined by many others. J. Kuschel, and G. Carrara measured values for lithium iodide; W. Hittorf, P. Walden, and C. Dempwolff, for sodium iodide; B. D. Steele, P. Walden, and C. H. Burgess and D. L. Chapman, for potassium tri-iodide. O. Gropp measured the effect of temp. on the conductivity of solid and frozen soln. of sodium iodide. For the effect of press. on the electrical properties, *vide* alkali chlorides. A. Reis found the **free energy** for the separation of the ions of KI to be 144 kilogrm. cals. per mol.; for NaI, 158; LiI, 153; and for HI, 305. S. W. Serkoff [35] measured the conductivity of lithium iodide in methyl alcohol; P. Walden, of sodium iodide in acetonitrile; P. Dutoit in acetone, benzonitrite, pyridine, acetophenone. J. C. Philip and H. R. Courtman, B. B. Turner, J. Fischler, and P. Walden of potassium iodide in methyl or ethyl alcohol; J. C. Philip and H. P. Courtman in nitromethane; P. Dutoit in acetone. H. C. Jones, of rubidium iodide in formamide. S. von Lasczynsky and S. von Gorsky, of potassium and sodium iodides in pyridine. A. Heydweiller found the **dielectric constants** of powdered and compact potassium iodide to be respectively 3·00 and 5·58.

According to K. von Hauer,[36] a soln. of potassium bromide sat. at 15° deposits almost all its bromide when repeatedly heated and cooled with an excess of potassium iodide; and potassium iodide dissolves in a sat. soln. of potassium chloride almost as copiously as in water. A. Étard has measured the mutual solubility of potassium bromide and chloride, potassium chloride and iodide, and potassium bromide and iodide, and found that the sum of the salts dissolved can usually be represented as a straight line when plotted with temp., and the vanishing point where the water has disappeared, coincides with the m.p. of the constituent with the lower m.p. The solubility of the ternary system: potassium chloride, bromide, and iodide, could not be determined as a function of temp. because the three salts cannot exist simultaneously in a sat. soln.—the chloride remains undissolved in the presence of the other two salts. G. J. Mulder (1864) found that the solubility of potassium iodide is diminished in the presenee of potassium sulphate. J. N. Brönsted measured the solubility of potassium iodide in soln. of potassium hydroxide of different conc.

A. Gérardin [37] measured the solubility of potassium iodide in *ethyl alcohol* of different conc. at 18°. He found 100 grms. of the aq. alcohol dissolved

Per cent. alcohol	5·2	9·8	23·0	38·0	59·0	86·0	91·0
Grams KI	130·5	119·4	100·1	76·9	48·2	11·4	6·2

According to P. Rohland, 100 grms. of *methyl alcohol* dissolve 16·5 grms. of potassium iodide at 20·5°; ethyl alcohol, 1·75 grms.; *propyl alcohol*, 0·46 grm. 100 grms. of absolute methyl alcohol at 22·5° dissolve 77·7 grms. of sodium iodide; absolute ethyl alcohol, 43·1 grms.; at ordinary temp. 100 grms. of methyl alcohol of sp. gr. 0·799 dissolve 83·3 grms. of sodium iodide; ethyl alcohol, sp. gr. 0·810, 58·8 grms.; and propyl alcohol, sp. gr. 0·816, 26·3 grms. H. C. Jones has shown that the mol. wt. of potassium, sodium, and ammonium iodides in methyl and ethyl alcohol, by the b.p. method, agree with the assumption that in the former solvent the salts are approximately 50 per cent. ionized, and in the latter, 25 per cent. The vap. press. determinations of these same soln. by O. F. Tower and A. F. O. German are in agreement with H. C. Jones' observations.

Glycol at 0° dissolves 31·03 per cent. of potassium iodide, and at 25°, 33·01 per cent., and the soln. have the respective sp. gr. 1·3954 and 1·3888. At 15·3° glycol also dissolves

28 per cent. of lithium iodide. Sodium iodide is very soluble in *acetone*, and 100 grms. of the solvent dissolve 3·08 grms. of sodium iodide at −2·5°; 2·38 grms. at 22°; 2·93 grms. at 25°; and 1·21 grms. at 56°; and P. Walden found at 0°, acetone dissolves 2·105 per cent. of potassium iodide, and at 25°, 1·302 per cent.—the sp. gr. of the two soln. are respectively 0·8227 and 0·7986; 100 c.c. of acetone dissolve 0·960 grm. of rubidium iodide at 0°, and 0·674 grm. at 25°. J. W. McBain and F. C. Coleman made an extensive study of the properties of soln. of sodium bromide in acetone. The mol. wt. is normal; on the other hand, with lithium iodide S. W. Serkov found evidence of the formation of complex salts. *Acetonitrile* at 0° dissolves 2·259 per cent. of potassium iodide, and at 25°, 2·003 per cent., and the two soln. have the respective sp. gr. 0·8198 and 0·7938. The same solvent at 0° dissolves 22·09 per cent. of sodium iodide, and at 25°, 18·43 per cent. 100 c.c. of acetonitrile dissolve 1·478 grms. of rubidium iodide at 0°, and 1·350 grms. at 25°. *Propionitrile* at 0° dissolves 0·0429 per cent. of potassium iodide, and at 25°, 0·0404 per cent., and the two soln. have the respective sp. gr. 0·8005 and 0·7821. The same solvent at 0° dissolves 9·09 per cent. of sodium iodide, and 6·23 per cent. at 25°. 100 c.c. of propionitrile dissolve 0·274 grm. of rubidium iodide at 0°, and 0·305 grm. at 25°. *Benzonitrile* at 25° dissolves 0·0506 per cent. of potassium iodide, and the soln. has a sp. gr. 1·0076. *Nitromethane* at 0° dissolves 0·315 per cent. of potassium iodide. and at 25° 0·307 per cent., and the respective sp. gr. are 1·1627 and 1·1367. the same solvent at 0° dissolving 0·34 per cent. of sodium iodide, and at 25°, 0·48 per cent. 100 c.c. of nitromethane at 0° dissolve 1·219 grms. of lithium iodide, and at 25°, 2·519 grms. 100 c.c. of nitromethane dissolve 0·567 grm. of rubidium iodide at 0°, and 0·518 grm. at 25°. 100 c.c. of *furfurol* at 25° dissolve 45·86 grms. of lithium iodide. Furfurol dissolves 25·1 per cent. of sodium iodide; and 4·94 per cent. of potassium iodide—the last-named soln. has a sp. gr. 1·2014. 100 c.c. of furfurol dissolve 4·930 grms. of rubidium iodide at 25°. *Benzaldehyde* at 25° dissolves 0·328 per cent. of potassium iodide, and the soln. has a sp. gr. 1·0446. *Salicylaldehyde* at 0° dissolves 1·093 per cent. of potassium iodide, and at 25°, 0·483 per cent., and the soln. have the respective sp. gr. 1·1501 and 1·1373. *Anisylaldehyde* at 0° dissolves 1·355 per cent. of potassium iodide, and at 25°, 0·644 per cent., and the soln. have the respective sp. gr. 1·1223 and 1·1180. *Methyl cyanoacetate* at 0° dissolves 2·827 per cent. of potassium iodide, and at 25°, 2·165 per cent., and the soln. have the respective sp. gr. 3·256 and 2·459. *Ethyl cyanoacetate* at 25° dissolves 0·0013 grm. of potassium iodide per 100 c.c. of soln. 100 grms. of *glycerol* dissolve 40 grms. of potassium iodide at 15·5°. *Pyridine* at 10° dissolves 0·26 per cent. of potassium iodide, and at 119°, 0·11 per cent. According to M. Stuckgold, a litre of *ethylurethane*, at 60°, dissolves 0·35 mol. of potassium iodide and 0·192 mol. of rubidium iodide. O. Aschan found that 95 per cent. *formic acid* liberates iodine from sodium iodide in the cold, but potassium iodide is stable.

A few properties of soln. of potassium iodide in water and in absolute methyl alcohol have been compared by W. Herz and G. Anders [38] at 25°. The solubility in grms. per litre are respectively 1029·8 and 132·6 grms.; the sp. gr. 1·7204 and 0·90187; the relative viscosities 1·193 and 0·872; the specific electrical conductivities 0·4812 and 0·0368; and the eq. conductivities 77·6 and 46·1 respectively. P. Dutoit and A. Levier have measured the electrical conductivities of soln. of sodium and potassium iodides in acetone; M. G. Levi and M. Voghera in pyridine; H. C. Jones, C. G. Carroll, and E. C. Bingham the conductivities and viscosities of sodium and potassium iodides in various solvents. M. Centnerszwer found the alkali halides do not dissolve in liquid cyanogen, but they do so in liquid hydrogen cyanide. Soln. of potassium iodide in liquid *hydrogen cyanide* have nearly four times the conductivity of soln. of this salt in water, the dielectric constant of this solvent is also greater than water, and hence the agreement with J. J. Thomson and W. Nernst's hypothesis of the cause of ionization. R. Lespieau obtained concordant results with the f.p. method. G. Bruni and A. Manuelli have measured the f.p. of soln. of potassium iodide in *succinic nitrile* and in *acetamide*, and the results agree with the assumption that ionization is complete in acetamide; the electrical conductivity is a maximum with a dilution of 30–40 litres per mol.; and the transport number of the anions in this solvent, 0·60, is rather greater than in water.

P. Walden [39] found that soln. of potassium iodide in *liquid sulphur dioxide* have an eq. conductivity at 0° of 44·5 reciprocal ohms when a mol. is dissolved in 15·3 litres; and of 99·0 in 760 litres—these results are rather smaller than with water. Similar results were obtained with sodium iodide 30·2 with a dilution $v=18·6$, and 35·1 with $v=60$. The raising of the b.p. of soln. of sodium iodide in liquid sulphur dioxide gave almost twice the theoretical value for the mol. wt. of NaI. With an ionized salt, the mol. wt. would be less than the theoretical value.

Hence it is inferred that the effect of ionization is marked either by polymerization: $2NaI \rightleftharpoons Na_2I_2$, or by the formation of complexes between solute and solvent: $NaI + nSO_2 = NaI.nSO_2$. Sulphur dioxide was found by C. J. J. Fox to be more soluble in soln. of sodium or potassium chloride, bromide, and iodide, and of rubidium iodide than in water alone; in sodium chloride soln. it is less soluble. This fact, in conjunction with P. Walden's observations (1899), is taken to mean that the iodides of sodium, potassium, and rubidium unite with sulphur dioxide to form complex salts, and P. Walden and M. Centnerszwer isolated a compound **potassium tetrasulphon-iodide,** $KI.4SO_2$, in red crystals by cooling a soln. of sulphur dioxide in a 20 per cent. soln. of potassium iodide. The f.p. of sulphur dioxide is depressed slightly from $-72.7°$ to a eutectic, and then rises to a maximum at -23.4 with about 8 mols. per cent.; during this period yellow crystals of a compound, **potassium tessaradecasulphon-iodide,** $KI.14SO_2$, are formed. The curve then rapidly falls to a second eutectic at about $-33°$, and rises to a second maximum at $0.26°$, corresponding with the formation of red crystals of the compound $KI.4SO_2$. No sign of **potassium monosulphon-iodide,** $KI.SO_2$, reported by E. Péchard, was observed on the f.p. or on the vap. press. curve; corresponding complexes, with sodium, ammonium, barium, calcium, and silver, were also reported by E. Péchard. The name *sulphone* was suggested for these bodies by P. Walden and M. Centnerszwer. F. Ephraim and I. Kornblum obtained **lithium monosulphon-iodide,** $LiI.SO_2$, and **lithium disulphon-iodide,** $LiI.2SO_2$, the former at 0°, the latter at lower temp.; he also obtained red **sodium disulphon-iodide,** $NaI.2SO_2$, at 0°, and pale yellow **sodium tetrasulphon-iodide,** $NaI.4SO_2$, in a freezing mixture, and he also obtained the corresponding red potassium compound, as well as lemon-yellow **rubidium tetrasulphon-iodide,** $RbI.4SO_2$, melting at 13.5°; and canary-yellow **cæsium tetrasulphon-iodide,** $CsI.4SO_2$. The dissociation temp. were also determined. R. de Forcrand and F. Taboury claim to have made sulphones of the type $MI.3SO_4$, where M represents an atom of sodium, rubidium, or cæsium; but F. Ephraim doubts this.

According to F. C. Franklin and C. A. Kraus,[40] *liquid ammonia* readily dissolves sodium and potassium iodides. The partial press. of ammonia in soln of potassium iodide at 25°, as measured by R. Abegg and H. Riesenfeld, is raised from 13.45 mm. of water to 13.28, and 14.88 mm. for $0.5N$-, N-, and $1.5N$-soln. respectively. H. M. Dawson and J. McCrae have shown that the distribution of ammonia between water and chloroform is generally lowered by the addition of various salts of the alkali metals and ammonium which they tried—halides, nitrates, chlorates, oxalates, sulphates, carbonates, hydroxides; this means that the solvent power of aq. soln. of the alkali salts is in general less than that of pure water—lithium chloride, ammonium bromide, and sodium iodide act in the opposite way. The other halide salts of lithium were not tried. The change produced in the partition coeff. by the halides, at 20°, is as follows:

	K	Na	NH_4	Li
Iodides	1.02	−0.32	—	—
Bromides	2.13	1.04	−0.35	—
Chlorides	3.18	2.04	0.88	−1.46

The increase produced by lithium and sodium halides is supposed to be connected with the formation of complex salts.

Potassium iodide is coloured sky-blue when heated in a sealed tube with the vapours of potassium or sodium. The salt is also coloured by cathode rays.[41] The decomposition of soln. of the alkali iodides by exposure to radium radiations, and ultra-violet light increases with increasing conc. A. Kailan supposed the radiations decompose the undissociated iodide liberating iodine and hydrogen both in acid and in alkaline soln. Aq. soln. of the alkali iodides are neutral, but, as O. Loew[42] has shown, the soln. gradually acquires a yellow colour and an alkaline reaction when kept for say 8 to 10 days; if air be excluded, the soln. remained colourless for 4 months. A. Houzeau attributed the effect to the presence of traces

of ozone in the air. M. Vidan believes that light alone, not air, effects the change. A. R. Leeds found a soln. acidified with hydrochloric or sulphuric acid is decomposed in sunlight with the separation of iodine, and that the quantity of iodine so liberated is proportional to the conc. of the soln. and the time of exposure. The slow decomposition of soln. of potassium iodide has been attributed to the carbon dioxide in the air which displaces a little hydriodic acid, which in turn is decomposed by the light, and M. Battander that the silica dissolved by the water from glass vessels plays the same *rôle* as carbon dioxide. In some recorded observations, it is not clear if the iodide was quite free from iodate, which facilitates tbe decomposition of potassium iodide. G. Papasogali found that purified potassium iodide soln. are not decomposed by **carbon dioxide**, but they are decomposed if iodates be present, the presence of alkali carbonates retards the reaction. G. Papasogali also found that light—direct or indirect—does not decompose the iodide, or a mixture of the iodide and iodate. As M. A. Houzeau has shown, **ozonized air** readily decomposes a soln. of potassium iodide, but C. Engler and A. Nasse observed no sign of a chemical reaction when dry ozone acts on dry potassium iodide. The effect of ozone on soln. of potassium iodide has been discussed in connection with ozone, and hydrogen peroxide. According to C. Weltzien, the last-named reagent forms potassium hydroxide and iodine. V. L. Bohnson studied the catalytic decomposition of **hydrogen peroxide** by sodium iodide in various solvents.

When potassium iodide is heated in a stream of air at 230°, or melted in a stream of carbon dioxide, some iodate is produced; and at 400°–500° M. Berthelot[43] found a little oxygen is absorbed and the iodate is formed. Consequently, the displacement of iodine by oxidizing agents is effected mainly when the iodide is in soln. R. Schindler found that when **water vapour** is passed over heated potassium iodide, hydrogen iodide and potassium hydroxide are formed. According to C. F. Schönbein,[44] crystals of potassium iodide are coloured yellow by **sulphur dioxide** and the colour fades away on exposure to air; the yellow colour produced in soln. of potassium iodide is not removed by exposure to air, by potassium hydroxide, or by ammonia. Liquid sulphur dioxide dissolves the iodides, forming yellow soln. The acid anhydrides—**sulphur trioxide, silica, boric, arsenic oxide, chromic oxide, and ferric oxide**—at a red heat in air, form the corresponding potassium salts and liberate iodine.[45] Sulphur trioxide or fuming sulphuric acid gives hydrogen sulphide, sulphur, sulphur dioxide and iodine, potassium sulphate is formed. H. Jackson represented the reaction when the sulphuric acid is present in large excess by the equation: $2KI+3H_2SO_4=I_2+SO_2+2KHSO_4+2H_2O$; and when there is just sufficient sulphuric acid to satisfy the potassium iodide: $8KI+9H_2SO_4=4H_2O+H_2S+4I_2+8KHSO_4$. To fulfil these reactions it is necessary, before bringing the two bodies into contact, that the sulphuric acid be boiling so as to fill the upper part of the flask with sulphuric acid vapour, and thus ensure the complete oxidation of the hydriodic acid first formed.

Hypochlorous acid converts potassium iodide into the chloride, iodate, and iodine. According to C. W. Hempel, **potassium permanganate** transforms acid or neutral soln. into iodates: $KI+2KMnO_4+H_2O=KIO_3+2KOH+2MnO_2$. C. F. Mohr found **potassium ferricyanide** oxidizes a conc. soln. of potassium iodide liberating iodine and forming the ferrocyanide, the reverse reaction occurs in dil. soln.; if barium hydroxide is present, barium iodate is formed. When potassium iodide is melted with **potassium chlorate** or **potassium nitrate**, or with **barium nitrate** or **barium dioxide**, it is oxidized to the iodate. According to A. Vogel,[46] a mixture of **ammonium chloride** and potassium iodide absorbs moisture from moist air, and becomes brown; if the mixture be heated, ammonium iodide and iodine are given off while a mixture of potassium chloride and iodide remains. J. P. Emmet obtained similar results with **ammonium nitrate**. F. Ephraim found that **lithium tetrammino-iodide** has a dissociation press. of 760 mm. at 90·5°. The alkali halides readily unite with many other salts, forming additional compounds. Compounds of **arsenious oxide** with the alkali halides have been described by J. P. Emmet[47]—

$2KI.3As_2O_3.H_2O$—and E. Harms—$2KI.6KAsO_2.3H_2O$ and $KI.2As_2O_3.KOH$. H. Schiff and F. Sestini supposed these products were mixtures. F. Rüdorff described the compound $KI.2As_2O_3$, and H. L. Wheeler the series $3CsX.2AsX_3$ and $CsX.As_2O_3$, where X represents an atom of the halogen, chlorine, bromine, or iodine.

The polyiodides, and the chloro- and bromo-iodides.—An aq. soln. of one of the alkali iodides dissolves considerable quantities of iodine,[48] and this the more, the greater the amount of iodine in soln. Thus, at 7°, soln. of potassium iodide dissolve the following proportions of iodine :

Per cent. KI . . .	1·802	4·628	7·201	10·036	11·893	12·643
Per cent. I . . .	1·173	3·643	6·037	8·877	11·182	12·060
Sp. gr. . . .	1·0234	1·0668	1·1112	1·1637	1·2110	1·2293

The increased solubility is due to the formation of polyiodides, and evidence of the existence of iodides as high as the enna-salt, KI_9, has been previously discussed. The tri-iodides of potassium, rubidium, and cæsium have all been isolated. The m.p., temp. of whitening, and the axial ratios of the crystals of potassium, rubidium, and cæsium tri-iodides are indicated—Table XXXI—*vide* Fig. 19, **2.** 19, 16.

TABLE XXXI.—THE ALKALI TRI-IODIDES.

	M.p.	Decomposition by whitening	Sp. gr.	Crystal system.	Axial ratios $a:b:c$.
KI_3 . .	38°	225°	3·498 (15°)	monoclinic	1 : 1·4154 : ? ; β=86° 37½′
RbI_3 .	190°	270°	4·03 (22°)	rhombic	0·6858 : 1 : 1·1234
CsI_3 .	201°–208°	330°	—	rhombic	0·6824 : 1 : 1·1051

In 1877 G. S. Johnson[49] prepared crystals of **potassium tri-iodide**, KI_3, by saturating an aq. or alcoholic soln. of potassium iodide with iodine, and evaporating the soln. slowly over sulphuric acid—the first crop of crystals were cubes of potassium iodide coloured with iodine ; in some days, dark blue, almost black, lustrous crystals belonging to the monoclinic system were formed, which, on analysis, had a composition corresponding with KI_3. H. L. Wells and H. L. Wheeler obtained similar crystals by dissolving the theoretical amount of iodine in a hot sat. soln of potassium iodide, and exposing the resulting soln. to a winter's temp. F. Ephraim found the dissociation press. rose from 80 mm. at 91°, to 261 mm. at 131°, to 695 mm. at 169°. **Rubidium tri-iodide,** RbI_3, and **cæsium tri-iodide,** CsI_3, were prepared by H. L. Wells and H. L. Wheeler in a similar manner. The two latter tri-iodides crystallize in the rhombic system. The crystals of all three tri-iodides are black. F. Ephraim found the dissociation press. of cæsium tri-iodide rose from 20 mm. at 159° to 160 mm. at 206°, to 345 mm. at 237°. There are two distinct curves which intersect at 207·5°, the m.p. By extrapolation, the dissociation press. is 760 mm. at 250°. For rubidium tri-iodide, the dissociation press. at 166° is 300 mm. ; at 173·5°, 376 mm. ; at 182°, 515 mm. ; at 196°, 600 mm. ; and at 200·5°, 700 mm. The salt melts between 182° and 196°. The cæsium salt is very sparingly soluble in water—100 c.c. of soln. contained 0·97 grm. of CsI_3 at 20°, and the sp. gr. of the liquid is 1·154 ; 100 c.c. of soln. contained 161 grms. of RbI_3, and the sp. gr. of the liquid was 2·19. M. Berthelot found the heat of formation of potassium tri-iodide : $KI+I_2=KI_3$, is zero with both constituents solid, with gaseous iodine the heat of formation is 10·8 Cals. at 0°, and with the salts in soln. and gaseous iodine, 10·2 Cals. The electrical conductivity and lowering of the f.p.[50] agree with the assumption that the tri-iodides are salts of a *hydrotri-iodic acid*, HI_3, with tervalent iodine atoms :

$$\begin{matrix} I \\ I \end{matrix}{>}I-H$$

Cæsium dichloro-iodide, $CsICl_2$, is made by adding a gram-atom of iodine to a soln. of a mol. of cæsium chloride in ten times its weight of water. The liquid is heated nearly to boiling and chlorine passed into the liquid until the iodine just dissolves. On cooling, pale orange rhombohedral crystals of cæsium dichloro-iodide are obtained. If an excess of chlorine is used *cæsium tetrachloro-iodide*, $CsICl_4$, is formed. If a large excess of cæsium chloride be present in soln. deep orange rhombic crystals are formed. R. W. G. Wyckoff could not make the rhombic crystals; he found the sp. gr. of the rhombohedral form to be 3·86, and the X-radiogram shows the space lattice is a body-centred rhombohedron in which the cæsium atom is placed either at the centre or corner, and the iodine atom at the corner or centre—the nearly equal scattering power of the atom of cæsium and iodine prevents a decision being made between these alternatives. Two chlorine atoms lie on the long diagonal nearly 0·31 of its length from the corners. F. Ephraim found the dissociation press. of $CsICl_2$ to be 24 mm. at 112°; 185 mm. at 166°; 640 mm. at 204·5°; and 760 mm. at 209°. F. Ephraim found the dissociation press. of **rubidium dichloro-iodide,** $RbICl_2$, to be 80 mm. at 97°; 403 mm. at 134°; and 600 mm. at 161°. **Potassium dichloro-iodide,** $KICl_2$, has also been prepared; but this salt is very unstable. F. Ephraim found the dissociation press. of $KICl_2$ at 41° to be 28 mm.; at 90°, 210 mm.; and at 136°, 704 mm. M. N. Rae made the dichloro-iodides by exposing the dry powdered iodide to the action of chlorine for some days, until the weight of the product corresponded with that required for the desired salt. If the action be continued longer, tetrachloro-iodides are formed. The **chlorodi-iodides,** MI_2Cl, have not been prepared. **Cæsium chloro-bromo-iodide,** CsIBrCl, was made by dissolving about one-fourth the theoretical amount of bromine and iodine in a warm soln. of cæsium chloride in five parts of water. On cooling, the salt separates out in yellowish-red crystals. An excess of cæsium chloride is necessary or the crystals will be too rich in bromine and poor in chlorine. If recrystallized the salt changes in composition, and it may be a mixture of isomorphous $CsIBr_2$ and $CsICl_2$. This statement, however, does not apply to the **rubidium chlorobromo-iodide,** RbIBrCl, which forms fine crystals when a warm soln. of 27 grms. of bromine, 42 grms. of iodine in 40 grms. of a sat. soln. of rubidium bromide is cooled. The salt can be recrystallized from water. The potassium salt has not been made. The m.p., temp. of whitening by decomposition, and the axial ratios of the rhombic crystals of the tri-iodides, chloro-iodides, and bromo-iodides are indicated in Table XXXII.

TABLE XXXII.—ALKALI TRIHALIDES—BROMOCHLORIDES AND CHLORO-IODIDES.

	M.p.	Decomposition by whitening.	Axial ratios $a:b:c$.
$KICl_2$	60°	215°	0·7335 : 1 : 1·2204
$RbICl_2$	180°–200°	265°	0·7341 : 1 : 1·1963
$CsICl_2$	225°–230°	290°	0·7373 : 1 : 1·1920
RbIBrCl	205°	200°	0·7271 : 1 : 1·1745
CsIBrCl	225°–235°	290°	0·7230 : 1 : 1·1760
$KIBr_2$	60°	180°	0·7158 : 1 : 1·1691
$RbIBr_2$	225°	265°	0·7130 : 1 : 1·1640
$CsIBr_2$	243°–248°	320°	0·7203 : 1 : 1·1667
CsI_2Br	—	—	0·6916 : 1 : 1·1419

If a gram-atom each of iodine and bromine be mixed with a warm very conc. soln. containing a mol. of potassium bromide, H. L. Wells and H. L. Wheeler found when the soln. is exposed for some time to a low temp., crystals of **potassium dibromo-iodide,** KBr_2I, are formed. F. Ephraim found the dissociation press. of $KIBr_2$ to be 5 mm. at 17°; 15 mm. at 40°; 47 mm. at 54·5°; 98 mm. at 71°;

and 140 mm. at 80°. F. Ephraim obtained a rather lower m.p. than did H. L. Wells and H. L. Wheeler. The latter also prepared by a similar process the corresponding **cæsium dibromo-iodide,** $CsBr_2I$, and **rubidium dibromo-iodide,** $RbBr_2I$. F. Ephraim found the dissociation press. of $CsIBr_2$ is 45 mm. at 157°; 160 mm. at 189·5°; 600 mm. at 235°; and 760 mm. at 242·5°. The corresponding rubidium salt, $RbIBr_2$, has a dissociation press. 87 mm. at 63°; 412 mm. at 93·2°; 608 mm. at 101·5°; and 760 mm. at 105·5°. When a gram-atom of iodine is added to a soln. of a mol. of cæsium bromide in 3 parts of a mixture of water with half its volume of alcohol, a crop of crystals of **cæsium bromodi-iodide,** $CsBrI_2$, is obtained. F. Ephraim found the dissociation press. of $CsBrI_2$ is 290 mm. at 172°; 511 mm. at 191°; and 655 mm. at 200°. The dissociation press. at 201·5° is 760 mm. The m.p. is 195·5°. The corresponding rubidium and potassium compounds could not be prepared. M. N. Rae made the dibromo-iodides by exposing the dry powdered iodine to the action of bromine vapour. The bromination did not extend to the pentahalide condition as when chlorine is used. No success was obtained with sodium iodide, while potassium, ammonium, rubidium, and cæsium iodides formed the salts, $MIBr_2$.

H. L. Wells and H. L. Wheeler (1892) prepared **cæsium penta-iodide,** CsI_5, as a black liquid, which solidified at about 73°, by heating cæsium tri-iodide with water, or solid iodine with a soln. of cæsium iodide. If a conc. alcoholic soln. of the impure solid be treated with two eq. of iodine, and cooled, triclinic black crystals of the penta-iodide are formed with axial ratios $a:b:c=0·9890:1:0·42765$. H. M. Dawson and E. E. Goodson isolated a compound of **sodium penta-iodide,** $NaI_5.2C_6H_5NO_2$, from a nitrobenzene soln. of iodine and sodium iodide.

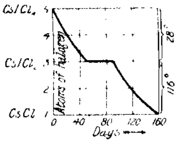

Fig. 34.—Decomposition Curve of $CsICl_4$.

In 1839, E. Filhol[51] reported that he had prepared **potassium tetrachloro-iodide,** KCl_4I, and the corresponding ammonium and magnesium salts, but did not succeed in making analogous compounds with sodium and a number of the common metals. H. L. Wells and H. L. Wheeler also prepared slender needles of E. Filhol's potassium salt, belonging to the monoclinic system, and with axial ratios $a:b:c=0·9268:1:0·44735$, $\beta=84°\ 18'$. H. L. Wells and H. L. Wheeler made the whole series of the alkali tetrachloro-iodides. They are most conveniently made by passing a large excess of chlorine into a conc. soln. of the iodide of the metal, and evaporating the soln. in a desiccator charged with chlorine, *e.g.* pale orange slender prisms of **cæsium tetrachloro-iodide,** $CsCl_4I$, belonging to the monoclinic system, with axial ratios $a:b:c=0·9423:1:0·4277$, $\beta=86°\ 20'$. Orange-yellow plates of **rubidium tetrachloro-iodide**, $RbCl_4I$, belong to the monoclinic system with axial ratios $a:b:c=1·1390:1:1·975$, $\beta=67°\ 6\frac{1}{2}'$. Slender needle-like rhombic crystals of **dihydrated sodium tetrachloro-iodide**, $NaCl_4I.2H_2O$, with axial ratios $a:b:c=0·6745:1:0·5263$. The crystals are rapidly decomposed by exposure and by treatment with alcohol or ether. W. N. Rae prepared the anhydrous **sodium tetrachloro-iodide,** $NaICl_4$, by exposing dried sodium iodide to the action of dried chlorine. H. L. Wells and H. L. Wheeler prepared long yellow deliquescent needle-like crystals of **tetrahydrated lithium tetrachloro-iodide,** $LiCl_4I.4H_2O$. The crystals are very unstable. W. N. Rae's analyses correspond with $LiCl_4I.3H_2O$; he made it by exposing lithium iodide, $LiI.3H_2O$, to the action of chlorine. W. N. Rae found that if the salts be placed in a desiccator over potassium hydroxide, and weighed at intervals of a few days, temp. constant, 28°, the pentahalides—CsI_5, $CsICl_4$, etc.—lose iodine steadily for about 60 days when the weight remains almost constant and the residue has a composition corresponding with the trihalide; the temp. is then raised, and there is again a steady loss until the composition corresponds with the normal halide. Fig. 34 typifies the results obtained with the cæsium penta-iodide and tetrachloro-iodide. In the

latter case the reactions are: $CsICl_4=CsICl_2+Cl_2$; and $2CsICl_2=2CsCl+I_2+Cl_2$ or $CsICl_2=CsCl+ICl$. In all cases tried, the final solid residue always contained the halogen of the smallest at. wt., making it appear as if this halogen and the metal are united by their primary valencies, the other halogen atoms by the secondary valencies:

$$\left[\begin{matrix} Cl\,. & & .\,I \\ & Cs & \\ Cl\,\cdot & & \cdot\,Cl \end{matrix}\right]Cl \qquad \left[\begin{matrix} & Cl \\ Cs\,. & \\ & I \end{matrix}\right]Cl$$

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§ 20. Ammonium Iodide

Ammonium iodide is formed when equal volumes of hydrogen iodide and ammonia are mixed together, and a soln. is obtained by neutralizing hydriodic acid with ammonia or ammonium carbonate ; or by treating ferrous iodide, FeI_2, with ammonium carbonate, as in the case of ammonium bromide. G. J. Jacobsen [1] made it by double decomposition of potassium iodide and ammonium sulphate, and separated the ammonium iodide and potassium sulphate by taking advantage of the great solubility of ammonium iodide and the low solubility of potassium sulphate in alcohol.

Boiling soln. of the two salts are mixed together, and after cooling, alcohol eq. to 15 per cent. of the water present is added. After standing, the clear liquid is separated from the crystals of potassium sulphate, and evaporated until the ammonium iodide commences to crystallize out, when ammoniacal alcohol is added and the crystals of potassium sulphate again removed. The ammonium iodide can then be separated by crystallization. The ammonium iodide is extracted from the mother liquid by dil. alcohol.

According to T. C. N. Broeksmit and E. Rupp, ammonium iodide is made from ammonia and iodine, in the presence of hydrogen peroxide : $2NH_3+I_2+H_2O_2=2NH_4I+O_2$:

Shake 10 parts of powdered iodine with 60 parts of pharmaceutical hydrogen peroxide, and gradually add 30 parts of aq. ammonia. If necessary hydrogen peroxide is added until the further evolution of gas does not occur, and the soln. has acquired a pale yellow colour. The filtered soln. becomes colourless when warmed on a water-bath, and after evaporation, the salt is rubbed with a little aq. ammonia, and dried.

A. Beyer treated potassium iodide with tartaric acid, and filtered off the precipitated $KH_5C_4O_6$. The soln. was neutralized with ammonium carbonate and evaporated. According to A. Gayard, ammonium iodide is formed during the decomposition of nitrogen iodide in light ; and by the action of iodide on aqua ammonia. F. Raschig states that if liquid ammonia is sat. with iodine at −10°, $(NH_3)_5I_2$ is formed, and this when warmed in contact with water forms ammonium iodide. This salt is also formed by the decomposition of ammonium hypoiodite.

Ammonium iodide forms deliquescent, *colourless* **crystals**—*pentagonal icositetrahedra*—belonging to the cubic system. J. W. Retgers [2] found that cubic crystals are obtained from water, and water containing urea ; while octahedral crystals are deposited from soln. containing ferric or chromic chloride, and lead iodide. According to B. Gossner, ammonium iodide forms isomorphous mixtures with the chloride over a very limited range. R. C. Wallace found that ammonium iodide does not show any signs of a transformation such as occurs with the bromide at 109° and with the chloride at 159°, but F. E. C. Scheffer found evidence of a transition point with ammonium iodide between −20° and −14°, and with a catalyst, between −17·2° and −15·6°—say, at −15°, while P. W. Bridgman found a transition point at −17·6°, corresponding with a vol. change of 14 per cent., and a latent heat of transformation of 2·05 kgrm. metres per grm. The effect of press. on the

transition temp. is illustrated in Fig. 35, and Table XXXIII. G. Bartlett and I. Langmuir showed that the **X-radiogram** of ammonium iodide at 20° shows a simple cubic lattice with like ions $5{\cdot}09\times10^{-10}$ cm. apart, and unlike ions $3{\cdot}60\times10^{-10}$ cm. apart. L. Vegard has worked out the X-radiogram of ammonium and tetramethylammonium iodides; the crystals of the former belong to the cubic system, those of the latter to the tetragonal system. The side of the elementary cube in the former case is $4{\cdot}54\times10^{-8}$ cm.; and the width of the base and the height of prism in the latter case are respectively $6{\cdot}26\times10^{-8}$ cm. and $4{\cdot}52\times10^{-8}$ cm. The elementary lattice of ammonium iodide is composed of 4I, 1N, and 12H lattices; and that of tetramethylammonium iodide of 2I, 2N, 8C, and 24H.

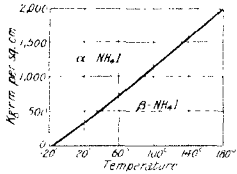

FIG. 35.—Effect of Pressure on the Transition Temperature of Ammonium Iodide.

The reported **specific gravity** of ammonium iodide[3] ranges from H. G. F. Schröder's 2·443 to H. Schiff and U. Monsacchi's 2·5168 (15°). The best representative value may be taken as 2·511. The **molecular volumes** of the ammonium halides come between those of rubidium and cæsium halides; for example, ammonium chloride, 34·01; ammonium bromide, 39·62; ammonium iodide, 57·51. W. Biltz has also studied the mol. vol. of this salt.

Ammonium iodide sublimes when heated, and the sublimate is freed from decomposition products only when air is excluded, otherwise it is coloured yellow by iodine or polyiodides. The **vapour density** of the salt corresponds with its decomposition into ammonia and hydrogen iodide, and of hydrogen iodide into

TABLE XXXIII.—TRANSITION TEMPERATURE OF AMMONIUM IODIDE.

Press. atm.	Transition temp.	Change in vol. c.c. per grm.	Latent heat kgrm.-m per grm.
1	−17·6°	0·0561	2·05
245	0·0°	0·0554	2·02
503	20·0°	0·0547	1·99
1171	80·0°	0·0528	1·84
2118	200·0°	0·0504	1·50

iodine and hydrogen. The dissociation of hydrogen iodide at 350° and 380 mm. press. is very slow, for it amounts[4] to about 4 per cent. in 24 hours' time. H. St. C. Deville and L. Troost's values, at 440° and 860°, are respectively 2·59 and 2·78—the theoretical value for the mixture NH_3+HI is 2·50, air unity. According to A. Smith and R. P. Calvert, the **dissociation temperature** at 760 mm. press. is 404·9° and the observed results can be represented by the expression: $\log p = -7714{\cdot}591/T - 10{\cdot}04345 \log T + 42{\cdot}69560$. A. Smith and R. H. Lombard find the vapour densities in grms. per c.c.:

	300°	320°	340°	360°	380°
Dissoc. press.	48·5 (310°)	143·5	135·6	235·7	407·3
Vapour density	0·000181	0·000307	0·000488	0·000874	0·00129
Latent heat	18·0	20·4	22·8	23·6	24·8

The theoretical vapour density curves calculated for complete dissociation (a), and for the undissociated vapour (b) are shown in Fig. 36 by dotted lines; the observed vapour density curve (continuous) shows that below 340°, the observed density of the sat. vapour is greater than the value required for no dissociation, meaning that the vapour is associated, but part of the vapour is probably also dissociated as well,

so that on the assumption that the associated molecule is $(NH_4)_2I_2$, the equilibrium condition is $(NH_4I)_2 \rightleftharpoons 2NH_4I \rightleftharpoons 2NH_3 + 2HI$, where the course of the curve shows that as the temp. rises, the amount of association decreases and the amount of dissociation increases. Although the observed density at 340° is normal, the ammonium iodide is here partly associated and partly dissociated. At the temp. in question, no secondary reaction producing hydrogen or nitrogen gases was observed—*e.g.* $2HI = I_2 + H_2$ and $3I_2 + 2NH_3 = 6HI + N_2$. The dissociation constants and the heats of dissociation of ammonium iodide could not be calculated on account of the association. If D_0 and D respectively denote the theoretical (undissociated) and the observed vapour densities of ammonium iodide; α the percentage number of dissociated NH_4I mols., and β the percentage associated, $\alpha - \frac{1}{2}\beta = (D_0 - D)/D$, from which α and β cannot be computed without another relation between the two unknowns. Assuming that all the NH_4I-mols. in the vapour have associated to $(NH_4)_2I_2$ or dissociated to $NH_3 + HI$, since $\alpha + \beta = 100$, then, at 300°, between 24 and 83 per cent. is associated and from 0 to 17 per cent. dissociated; at 380°, between 0 and 59 per cent. is associated, 11 to 41 per cent. dissociated.

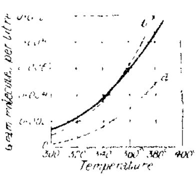

FIG. 36.—The Vapour Density Curves of Ammonium Iodide.

H. Rassow gave 551 ± 3° for the **melting point** of ammonium iodide; and G. Bartha, 220° for the **boiling point** in vacuo. The **latent heats of vaporization** calculated from

$$L = \frac{TP}{760}\left(\frac{7715}{0\cdot4343T^2} - \frac{10\cdot04}{T}\right)\frac{0\cdot02419}{D} \text{ Cals.}$$

are indicated above. According to J. Ogier,[5] the **heat of formation** from its elements, iodine solid, is 65·1 Cals.; according to M. Berthelot, iodine gaseous, 56 Cals.; and, according to J. Thomsen, 49·31 Cals. J. Thomsen also gives for the crystalline solid, $NH_3 + HI = NH_4I + 32\cdot46$ Cals. J. Thomsen's values for the **heat of solution** vary from −3·52 to −3·585 Cals. for a mol. of the salt in 200 mols. of water; and for the **specific heat** of a 3·9 per cent. soln., 0·963 at 18°.

The **solubility** of ammonium iodide [6] in water is very great. At −27·5°, the cryohydric temp., water dissolves 55 per cent. of the salt, and at 15°, 62·5 per cent. A contraction occurs when this salt dissolves in water. Thus, H. Schiff and U. Monsacchi [7] calculate from the **specific gravity** determinations of W. H. Perkin and W. W. J. Nicol:

Per cent. NH_4I .	3·355	13·42	30·50	54·64	60·44
Sp. gr. 15° . .	1·0202	1·0899	1·2341	1·5109	1·5948
Vol. 100 grms. .	98·0200	91·7515	81·0331	66·1844	62·7054
Vol. components	98·0542	91·9848	81·6768	67·1082	63·6079

According to W. Ostwald, the soln. of m grms. of the salt in $2000m$ grms. of water at 20° is attended by a contraction of 52·9 c.c. per mol. of salt. The **molecular volumes** of ammonium iodide in 10, 20, and 50 per cent. soln., calculated by J. Traube from F. Kohlrausch's sp. gr. data, are respectively 54·6, 55·2, and 56·2, when the mol. vol. of the solid is 59·3.

W. C. Röntgen and J. Schneider [8] have found the compressibility of soln. of a mol. of ammonium iodide in 700 mols. of water to be 0·954; and in 1500 mols. of water 0·910. The following table enables the values for the alkali and ammonium halides to be compared for soln. containing a mol. of the salt in 700 and 100 mols. of water:

TABLE XXXIV.—COMPRESSIBILITIES OF AQUEOUS SOLUTIONS OF THE ALKALI HALIDES.

	700 H_2O.						1500 H_2O.				
	H	NH_4	Li	K	Na		H	NH_4	Li	K	Na
I	—	0·910	0·888	0·869	0·863	I	—	0·954	0·940	0·932	0·924
Br	0·960	0·910	0·869	0·862	0·851	Br	0·981	0·953	0·934	0·930	0·923
Cl	0·949	0·901	0·858	0·848	0·837	Cl	0·974	0·945	0·928	0·919	0·917

W. C. Röntgen and J. Schneider also measured the **surface tension** of the soln. of ammonium iodide. F. H. Getman found the **viscosity** of soln. of this salt falls from 0·008577 dynes per cm. for 0·5*N*-soln. to a minimum 0·007779 dynes per cm. for 2·502*N*-soln.; and then rises to 0·009321 for 5·004*N*-soln. The respective sp. gr. of these soln. are 1·0447, 1·2304, and 1·4591. The viscosities of 1·001*N*-soln. falls from 0·01146 at 10° to 0·01031 at 15°, to 0·009277 at 20°.

The lowering of the **vapour pressure** of water by ammonium iodide measured by G. Tammann[9] shows that the fall is 12·5 mm. for ½*N*-soln.; 25·1 mm. for *N*-soln.; and 243·5 for 10*N*-soln. According to L. C. de Coppet, the soln. of a mol. of the salt in water lowers the temp. of maximum density 11·1°. The degree of ionization calculated by S. M. Johnston from the raising of the **boiling point** of water by normal soln. of ammonium iodide agrees with the value of N. Zelinsky and S. Krapiwin and S. Arrhenius from the **electrical conductivities** of soln. of a mol. of the salt in *v* litres of water:

v	16	32	64	128	256	512	1024
λ	125·4	129·6	133·4	135·9	138·7	141 3	143·7

At higher conc. there is evidence of the hydration of the solute. M. le Blanc found the **decomposition potential** of a *N*-soln. with platinum electrodes to be 0·88 volt, *i.e.* 0·25 volt smaller than the corresponding sodium and potassium salts. B. Holmberg found the law of mass action is applicable to the ionization of 0·05*N*- to *N*-soln. of sodium and potassium iodides. S. von Laszczynsky and S. von Gorsky measured the conductivity in pyridine soln.

The **molecular refraction,** dispersions, and **magnetic rotation,** measured by J. H. Gladstone and W. H. Perkin,[10] are respectively 39·66, 4·88, and 19·996. According to H. Topsöe and C. Christiansen, the **refractive index** of crystals of ammonium iodide for the *C*-line is 1·6938; for the *D*-line, 1·7031; and for the *F*-line, 1·7269. M. le Blanc and P. Rohland found for the mol. refraction of 12·5 per cent. soln. with the *D*-line, 40·01 by J. H. Gladstone and T. S. Dale's formula, and 23·39 by Lorentz and Lorenz's formula. O. Reinkober studied the reflexion spectrum for **ultra-red rays.**

Ammonium iodide is soluble in *methyl alcohol*, and N. Zelinsky and S. Krapiwin[11] have studied the electrical conductivity of these soln., and it was found that the ionization is much greater in the pure alcohol than in 50 per cent. soln. The soln. in *ethyl alcohol* is attended by a considerable contraction, and, according to W. H. Perkin, a 21 per cent. soln. of ammonium iodide in alcohol (sp. gr. 0·7947) has the sp. gr. 0·9413 at 15°, and the alcoholic soln. has a mol. magnetic rotation of 18·9. H. C. Jones and F. H. Getman measured the lowering of the f.p., and G. Carrara the electrical conductivity of alcoholic soln. which indicate an increasing ionization with increasing dilution, *vide* alkali iodides. Both G. Carrara and P. Dutoit and A. Levier have investigated the conductivity of soln. in *acetone*—with a dilute ion *v*=500, the degree of ionization is 0·61; with *v*=20,000, 0·98 and with *v*=50,000, 1·0. The results are in accord with the dilution law; the ionization constant is *K*=0·00165. M. G. Levi and M. Voghera found both ammonia and hydrogen were developed at the cathode during the electrolysis of soln. in *acetone* and in *pyridine*. S. von Laszczynsky and S. von Gorsky have also measured

the conductivity of soln. of this salt in pyridine. P. Walden and M. Centnerszwer found the conductivities and f.p. determinations of soln. of ammonium iodide in liquid *sulphur dioxide* corresponded with the assumption that a complex is formed ; and R. de Forcrand and F. Taboury found liquid sulphur dioxide forms *sulphones* of the type $MI.3SO_2$ with the iodides of sodium, rubidium, and caesium—the first is amorphous, the two latter crystallize from liquid sulphur dioxide at 0°.

H. Moissan found ammonium iodide to be soluble in liquid *ammonia*, while H. P. Cady, and E. C. Franklin and C. A. Kraus, showed that the conductivity of the soln. resembles that of the corresponding bromide. L. Troost prepared a series of ammino-compounds analogous with those of ammonium chloride and bromide, and the compounds behave in a similar manner. The dissociation press. of **ammonium ammino-iodide,** $NH_4I.NH_3$, or $HI.2NH_3$, is 10 mm. at −17° ; 57 mm. at 0° ; 455 mm. at 35° ; and 1140 mm. at 56°. **Ammonium triammino-iodide,** $NH_4I.3NH_3$, or $HI.4NH_3$, fuses at −12°, and its dissociation press. is 130 mm. at −27° ; 380 mm. at 0° ; 700 mm. at 14·6° ; 840 mm. at 19·5° ; and 1160 mm. at 30°. J. Kendall and J. G. Davidson measured the f.p. curve of mixtures of ammonia and ammonium iodide ; and isolated ammonium triammino-iodide, with a m.p. of −8° ; and **ammonium tetrammino-iodide,** $NH_4I{\cdot}4NH_3$, melting at −5·1°, but did not obtain L. Troost's mono-ammino-salt or his **ammonium hexammino-iodide,** $NH_4I.6NH_3$, or $HI.7NH_3$, melting at 28°, and with the dissociation press. 435 mm. at −29° ; 575 mm. at −21·2° ; 770 mm. at −12·8° ; and 1735 mm. at 11·4°. The stability of the ammonium ammino-halides increases with the at. wt. of the halogen.

Aq. soln. of ammonium iodide gradually assume a yellow colour on exposure, presumably owing to oxidation ; and, according to A. R. Leeds,[12] the reaction is accelerated by exposure to light. An hour's exposure to the electric light, sunlight, and magnesium light liberated respectively 15·0, 3·9, and 0·06 mgrm. of iodine from a soln. acidified with sulphuric acid ; and similarly 9·8, 2·3, and 0·07 mgrm. from a soln. acidified with hydrochloric acid. If air and oxygen be excluded, no iodine separates even with the most intense illumination. The vapour of sulphur trioxide, says H. Rose, is absorbed by ammonium iodide at ordinary temp., forming a product which decomposes with the evolution of sulphur dioxide, and a residual reddish-brown mass. P. Hautefeuille found ammonium iodide can be sublimed in hydrogen chloride without decomposition, but above 360° some ammonium chloride is formed. M. Berthelot did not find any indications of the formation of a hydroiodide by heating ammonium iodide with an excess of hydriodic acid (sp. gr. 2) at 280°.

According to G. S. Johnson,[13] dark-brown rhombic plates of **ammonium tri-iodide,** NH_4I_3, with axial ratios $a:b:c=0·6950:1:1·1415$ isomorphous with the alkali tri-iodides, are obtained by evaporating a sat. aq. soln. of iodine and ammonium iodide over sulphuric acid. The sp. gr. is 3·749. R. Abegg and A. Hamburger obtained good crystals by warming a sat. soln. of iodine with the calculated quantity of ammonium iodide, and slowly cooling the mixture. The dissociation press. $NH_4I_3 \rightleftharpoons NH_4I + I_2$ was estimated at 0·053 mm. by treating the salt with benzene at 25° ; no higher polyiodide exists at 25°. The crystals are slightly deliquescent, and they dissolve unchanged in a small proportion of water, but iodine separates when a large proportion of water is used. E. Filhol prepared **ammonium tetrachloro-iodide,** NH_4Cl_4I, in a similar manner to the corresponding potassium compound.

C. L. Jackson and I. H. Derby prepared **ammonium dibromo-iodide,** NH_4Br_2I, by treating ammonium bromide with an ethereal soln. of iodine bromide, and evaporating the ether ; and also by exposing ammonium iodide to the vapour of bromine when the salt is first coloured black and then scarlet. The black colour may represent an intermediate product. The dibromo-iodide is blood red by transmitted light, and green with a metallic lustre in reflected light. It smells of iodine bromide, and on long standing leaves a residue of ammonium bromide ; the same decomposition occurs to a limited extent when the salt is digested with ether.

When treated with water, bromine and iodine are set free; hydrochloric acid liberates iodine; sodium or ammonium hydroxides give a black precipitate of nitrogen iodide, and the mother liquid liberates bromine when treated with hydrochloric acid. Sulphurous acid gives hydrobromic and hydriodic acids. F. Ephraim found the dissociation press. of NH_4IBr_2 to be 65 mm. at 107°; 204 mm. at 134°; 465 mm. at 154°; and 640 mm. at 161°.

Dry iodine absorbs dry ammonia, forming a dark brown liquid from which the excess of ammonia can be removed by standing over conc. sulphuric acid. The same liquid is obtained by adding iodine to a sat. soln. of ammonium nitrate or carbonate with one-third an eq. of potassium iodide; as is also the case when a sat. soln. of potassium tri-iodide is treated with aq. potassium hydroxide and ammonium nitrate. F. Guthrie and W. H. Seamon[14] prepared these compounds. The analyses corresponds with NH_3I_2, so that these products were formerly regarded as **iodammonium iodide**, $(NH_3I)I$, or **ammino-iodine**, NH_3I_2; but, according to J. F. Norris and A. I. Franklin, the properties correspond with a mixture of nitrogen iodide, NHI_2, and ammonium polyiodide.

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§ 21. The Alkali Monosulphides

The union of sulphur with alkali, *nitrum*, has been known from early times. In the first century, Pliny, in his *Historia naturalis* (**31**. 46), refers several times to the combination *sal nitrum sulphuri*, formed by melting nitrum with sulphur in a vessel over a charcoal fire. It is mentioned by Geber. In the thirteenth century Albertus Magnus, in his *Alchymia*, described the preparation of this substance by fusing sulphur with the alkali, and by digesting sulphur with alkali lye. Basil Valentine described some of the properties of the soln. A. Libavius,[1] R. Boyle, J. R. Glauber, G. E. Stahl, and H. Boerhaave also investigated the properties of *hepar sulphuris—liver of sulphur*—or *hepar sulphuris salinum*, or *hepar sulphuris alkalinum*, as it was variously called by the alchemists of the Middle Ages. J. R. Glauber made it by calcining sodium sulphate with charcoal. J. Mayow found the soln. of alkali sulphide is oxidized to sulphate when exposed to air. G. E. Stahl called it *sulphur alcalico sali annexum*. The nature of *hepar sulphuris* has been investigated by J. J. Berzelius, C. L. Berthollet, H. Hager, R. Kemper, H. E Schöne, and many others. The corresponding *soda-liver of sulphur* has been investigated by L. N. Vauquelin, E. Filhol, and J. B. Senderens, etc. The results are discussed in connection with the alkali sulphides, and polysulphides. Liver of sulphur is not a chemical individual, but rather a mixture of many sulphur compounds of the alkalies.

Liver of sulphur is made by gently heating sulphur with potassium carbonate in closed earthenware or cast-iron crucibles, but less contaminated with impurities, in glass flasks. The product so obtained is a dull green mass; the freshly broken surfaces are liver-coloured—hence the name. Liver of sulphur is a mixture of various polysulphides, sulphate, thiosulphate, and may be some unattacked carbonate, particularly if less than 36 per cent of sulphur and a low temp. have been employed. The composition of the product depends on the proportions of the constituents and the temp. to which they have been heated. If higher proportions of sulphur be used the higher polysulphides predominate in the product. Liver of sulphur is used for making ointments in skin diseases; for internal and external application in rheumatism, etc. It is the *potassa sulphurata* of the Pharmacopœia; and it is used by gardeners as a fungicide and parasiticide.

According to G. Calcagni, 100 c.c. of a cold 66 per cent. of sodium hydroxide dissolves 24·55 grms. of sulphur or 57 parts of sulphur per 23 parts of sodium; while 100 c.c. of a similar soln. of potassium hydroxide dissolves 17·70 grms. of sulphur, or 59·35 parts of sulphur per 39·15 parts of potassium. The soln. reacts for sulphides, polysulphides, thiosulphates, and sulphites. The reaction between alkali hydroxides and sulphur is complex; probably sulphides are first formed from which thiosulphates are produced, and by the dissolution of more sulphur, polysulphides; the thiosulphates lose part of their sulphur forming sulphites. In the more conc. soln. of sulphur part of the latter appears to be uncombined because these soln. yield sulphur to hot benzene. All the soln. are decomposed by carbon dioxide yielding sulphur and hydrogen sulphide.

The preparation of the alkali monosulphides.—Products usually called sulphides have been obtained by the direct union of the elements. Thus, L. Troost[2] prepared what he regarded as amorphous **lithium sulphide**, Li_2S, by the action of sulphur vapour on heated lithium. H. Davy, and J. L. Gay Lussac and L. J. Thénard, prepared **sodium sulphide**, Na_2S, by warming sulphur with sodium;

and, according to G. C. Winkleblech, the reaction proceeds with incandescence at ordinary temp. **Potassium sulphide,** K_2S, was likewise prepared from its elements in a similar manner. M. Rosenfeld triturated the sulphur and sodium in a mortar, and modified the violence of the reaction by admixing the components with sodium chloride. R. Bunsen likewise found that rubidium or cæsium burns with incandescence in sulphur vapour, forming respectively **rubidium sulphide,** Rb_2S, and **cæsium sulphide,** Cs_2S. J. Locke and A. Austell boiled a soln. of sulphur in toluene or naphthalene with metallic sodium. C. Hugot dissolved the calculated quantity of sulphur in a soln. of sodium or potassium in liquid ammonia.

R. Bunsen and H. E. Schönn made sodium and potassium monosulphides by the action of sodium or potassium on sulphuric acid, heavy spar, carbon disulphide, and various other organic and inorganic sulphur compounds. The reaction is utilized in testing for sulphur in these products since the presence of a sulphide is readily recognized. H. Moissan prepared rubidium and cæsium sulphides by the action of molten sulphur or of hydrogen snlphide on the alkali hydrides. J. J. Berzelius found that a current of hydrogen will reduce red-hot potassium sulphate to the sulphide, and H. V. Regnault found that glass or porcelain tubes are thereby much attacked. C. Stammer also reported that the same salt is likewise reduced by carbon monoxide, but A. Levol could not confirm the statement. J. G. Willans has patented the reduction of salt cake by carbon monoxide and steam ; W. Weldon, by combustible gases.

P. Berthier and A. J. P. du Mênil obtained sodium or potassium sulphide by heating a mixture of four gram-atoms of coal with one mol. of sodium sulphate. This reaction was known to J. R. Glauber, and it probably dates much further back than this. L. Troost prepared lithium sulphide in an analogous manner. A. Mourlot obtained a crystalline mass of the sulphide—lithium, sodium, or potassium —by heating the mixture in Moissan's electric furnace for abont five minutes. The reduction of the sulphate has been recommended for the manufacture of the sulphide on a large scale. To facilitate the manipulation of the products, F. Jean sintered a mixture of sodium snlphate, barinm sulphate, wood charcoal, and coal. F. H. Gossage recommended mixing 30 per cent. of sodium chloride with the mixture to be reduced so as to lessen the attack on the firebricks. W. Weldon recommended the use of bricks of coke and graphite powder ; R. W. Wallace and C. F. Claus used a bauxite lining ; B. Peitzsch, iron vessels ; and P. Berthier, carbon crucibles. F. Ellerhausen has also paid special attention to the destructive action of hot sodium sulphide on furnace walls. According to J. L. Gay Lussac, much of the snlphate will remain undecomposed if the temp. be too low, and polysulphides will be formed ; C. Wittstock also found that if too little coal be used, a mixture of polysulphides and carbonate will be formed ; and A. Bauer found that polysulphides and carbonate are always found among the products of this reaction. J. L. Gay Lussac obtained a very combustible substance—*pyrophore de Gay Lussac*—by decomposing potassium sulphate with a large excess of carbon. It is said to be a mixture of polysulphides, potassium, and carbon. It behaves like the *pyrophore de Homberg* prepared with potash alum. Patents have been taken out for the reduction of salt cake to sulphide by coke or coal by A. R. Arrott, F. H. Gossage, J. Wilson, J. Barrow, C. F. Claus, etc. The process employed in Germany in 1880 is described by C. Winkler (1880)—*vide* sodium carbonate. P. Sabatier found that red-hot sodium sulphate is rapidly and energetically reduced by carbon disulphide vapour—but the product is a mixture, $2Na+1\frac{1}{2}S$.

J. J. Berzelius melted sulphur with an excess of potassium hydroxide and found the product to be a mixture of the monosulphide and thiosulphate. J. Kircher passed hydrogen sulphide over coarsely powdered sodium hydroxide at 100°. M. J. Fordos and A. Gélis made sodium sulphide by heating sodium carbonate with sulphur to 275° ; the product is obviously a kind of soda-liver of sulphur. J. W. Kynaston melted sodium hydroxide with calcium sulphide ; and J. V. Esop, and C. Vincent treated a soln. of barium or other sulphide with sodium or potassium

sulphate. C. T. Kingzett prepared sodium sulphide by the action of hydrogen sulphide on molten sodium chloride, and L. Bemelmans patented a process in which molten potassium chloride is run into molten sulphur—sulphur chloride is formed, potassium sulphide is obtained as a by-product.

P. Sabatier prepared anhydrous potassium sulphide by dehydrating the dihydrate in a stream of hydrogen gas; and anhydrous sodium sulphide by dehydrating the enneahydrate in a quick stream of hydrogen while it is heated on a sand-bath. The products are contaminated with silica from the glass. The dry methods of preparation furnish oxidized products—thiosulphates and polysulphides. Sometimes also some carbonate. E. Priwoznik recommended purifying sodium sulphide by digesting a conc. soln. with copper, and evaporating the soln. in a stream of hydrogen; and W. Gibbs recommended recrystallization from 90 per cent. alcohol. W. P. Bloxam has pointed out that while sodium thiosulphate is usually considered to be insoluble in alcohol, this is not the case when polysulphides are present. No solvent capable of separating thiosulphates and polysulphides is yet known.

When a hot aq. soln. of sodium sulphide, sp. gr. 1·285, is cooled, crystals of **enneahydrated sodium sulphide,** $Na_2S.9H_2O$, separate. This salt is the stable hydrate at ordinary temp. L. N. Vauquelin, and J. J. Berzelius made a soln. of alkali monosulphide by dividing a soln. of alkali hydroxide into two parts, one half is sat. with hydrogen sulphide, $KOH+H_2S=KSH+H_2O$; the two soln. are then mixed together: $KOH+KSH=K_2S+H_2O$. Sodium monosulphide is prepared in the following manner:

Dissolve 333 grms. of pure sodium hydroxide (made from the metal) in a litre of air-free water. Pour the soln. into a flask, and pass a rapid stream of washed hydrogen sulphide into the soln. through a wide glass tube (1 cm. bore) fitted into a double-bored stopper, so as to protect the contents of the flask from air as much as possible. The object of the wide delivery tube is to avoid choking the tube with the separated sulphide. There is an increase in the volume of the soln. such that 1000 c.c. become 1218 c.c. When the soln. is sat. the pale yellow liquid may be poured into small glass-stoppered bottles and sealed with paraffin; or the soln. may be evaporated in a platinum or porcelain dish until a film of crystals begins to form on the surface, and the hot liquid bottled and sealed. The *liquids may deposit crystals of sodium monosulphide—$Na_2S.9H_2O$—on standing or cooling.* The bottled soln. keep indefinitely when protected from the atm. air. A small quantity of black iron, nickel, or silver sulphide may settle on the bottoms of the bottles on standing. For use, the soln. is diluted to a sp. gr. 1·14. Sodium hydroxide pure by alcohol does not give so satisfactory a soln. as that prepared from the metal, since a soln. prepared from the former will be coloured with colloidal sulphides, which only separate after long standing. According to E. Prothière and A. Revaud, a layer of almond or olive oil on the surface of a soln. of the sulphide cuts off the air without forming deposits or an emulsion. The soln. then keeps indefinitely.

P. Sabatier, F. Lüthe, W. Helbig, H. Finger, W. P. Bloxam have also prepared crystals of enneahydrated sodium sulphide, by a method analogous to that employed by L. N. Vauquelin and J. J. Berzelius. R. Böttger proceeded in a similar manner, using alcohol soln. H. Pomeranz supposes that the primary action between alkali hydroxides and sulphur is analogous to that between alkali hydroxides and chlorine in the cold, and takes place according to the equation; $4NaOH+2S=Na_2S+Na_2SO_2+2H_2O$ or $3NaOH+2S=Na_2S+NaHSO_2+H_2O$. In support of this view, it is found that a mixture of sulphur and sodium hydroxide in the ratio 2S : 3NaOH has a similar bleaching action on *p*-nitro-aniline-red to that of sodium hyposulphite. Polysulphide and thiosulphate are only produced by the further action of the sulphur on the sulphide and hyposulphite.

The solubility of sodium sulphide in water, studied by N. Parravano and M. Fornaini, shows a cryohydrate temp.—10° when 9·34 per cent. of anhydrous sulphide is present in soln. The enneahydrate exists in aq. soln. up to 48·9°, where it is transformed into the **hemihenahydrated sodium sulphide,** $Na_2S.5\frac{1}{2}H_2O$, which exists in a labile condition between 48·9° and 91·5°, and is stable between 91·5° and 94°. The **hexahydrated sodium sulphide,** $Na_2S.6H_2O$, is stable between 48° and 91·5°; but the enneahydrate does not change into the hexahydrate at 48°, rather

does it pass into the 5½ hydrate at 48·9°. This is a rare case where the phenomenon observed in a transformation is accompanied by an absorption of heat. R. Böttger and P. Sabatier made what was probably the hemihenahydrate—they said pentahydrate—by melting the enneahydrate and slowly cooling the molten mass from 90°. G. Lemoine isolated the same hydrate from the products of the action of sodium hydroxide in phosphorus sulphide. C. Göttig reported the hemihenahydrate and the hexahydrate by the action of hydrogen sulphide on alcoholic soln. of sodium hydroxide. He obtained the hexahydrate between 17° and 22°, and the hemihenahydrate between 41° and 45°. H. Finger said that the needle-like crystals which separate when hydrogen sulphide is passed into a conc. soln. of sodium hydroxide are the hexahydrate. These crystals subsequently dissolve before the lye is all sat. with gas; and W. P. Bloxam believes these crystals have the empirical composition $2Na_2S.NaOH$. P. Sabatier obtained crystals of what he regarded a *hemi-enneahydrated sodium sulphide*, $Na_2S.4\frac{1}{2}H_2O$, by keeping the enneahydrate in vacuo over sulphuric acid. The individuality of this hydrate and of *trihydrated sodium sulphide*, $Na_2S.3H_2O$, described by A. Damoiseau, has not been confirmed

W. P. Bloxam conc. a soln. of potassium hydroxide, half sat. with hydrogen sulphide, in vacuo over calcium chloride, and obtained small white tabular crystals of **dodecahydrated potassium sulphide,** $K_2S.12H_2O$. The mother liquor furnished brilliant four-sided flat rhombs of **pentahydrated potassium sulphide,** $K_2S.5H_2O$, analogous with the crystals obtained by H. E. Schöne and J. J. Berzelius when these crystals are repeatedly powdered, and exposed in vacuo over sulphuric acid; W. P. Bloxam obtained **dihydrated potassium sulphide,** $K_2S.2H_2O$; P. Sabatier also prepared the dihydrate. W. Biltz and E. Wilke-Dörfurt prepared white crystals of **tetrahydrated rubidium sulphide,** $Rb_2S.4H_2O$, by precipitation from the aq. soln. by the addition of alcohol and ether—an oil first separates which subsequently crystallizes—and also by evaporating the conc. aq. soln. in a desiccator over calcium chloride. When these crystals are dehydrated at 200°, they form white crystals of **dihydrated rubidium sulphide,** $Rb_2S.2H_2O$, and when heated to a still higher temp., they ultimately give the anhydrous salt. W. Biltz and E. Wilke-Dörfurt prepared white crystals of **tetrahydrated cæsium sulphide,** $Cs_2S.4H_2O$, exactly like the corresponding rubidium salt.

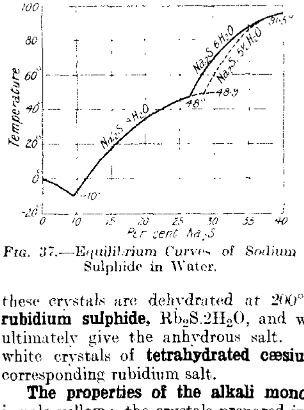

FIG. 37.—Equilibrium Curves of Sodium Sulphide in Water.

The properties of the alkali monosulphides.—Amorphous lithium sulphide is pale yellow; the crystals prepared in the electric furnace by A. Mourlot [3] were small cubes without action on polarized light. The crystals of anhydrous sodium sulphide prepared by the dry processes are more or less impure, and this determines largely the colour which is variously reported, white, yellow, and red. Sodium enneahydrate forms colourless tetragonal crystals which, according to C. F. Rammelsberg, have the axial ratio $a:c=1:0·982$. The colourless crystals of the enneahydrate become yellow in air, presumably owing to the formation of polysulphides, but H. Kolbe says the yellow crystals become white again when heated, presumably owing to the oxidation of the yellow product. The crystals of anhydrous potassium sulphide are red, and they become black on melting. According to C. Wittstöck, the red crystals are coloured by impurities—polysulphides. Both P. Berthier and P. Sabatier prepared colourless crystals. The crystals obtained by evaporating the soln. in a stream of hydrogen sulphide are colourless. H. E. Schöne and W. P. Bloxam say the pentahydrate forms colourless glass-like four-sided flat

prisms; W. P. Bloxam says the dodecahydrate forms colourless glass-like tabular crystals. W. Biltz and E. Wilke-Dörfurt say that the hydrates of rubidium and cæsium sulphides form white crystals, and that anhydrous rubidium sulphide, Rb_2S, is dark red—presumably owing to the presence of impurities. Sodium, potassium, rubidium, and cæsium sulphides are all deliquescent, and this the more the greater the at. wt. of the alkali metal. P. W. Bridgman found that potassium monosulphide is dimorphic at atm. press. The transition temp. is 146·4° at atm. press., and no other modification was found at 20° and at 200° with respectively 12300 and 12000 kgrms. per sq. cm. press.:

Press. . .	1	1000	3000	5000 kgrm. per sq. cm.
Transition temp.	146·4°	158·4°	182·4°	206·4°
Change of vol. .	0·000948	0·000918	0·000835	0·000794 c.c. per grm.
Latent heat .	0·331	0·330	0·324	0·317 kgrm.-m. per grm.

The low temp. form is the more expansible, and has the higher sp. ht. The **specific gravity** of crystalline lithium sulphide, according to A. Mourlot, ranges from 1·63 to 1·70; E. Filhol gives 2·471 for sodium sulphide, and 2·13 for potassium sulphide—E. Filhol's numbers presumably refer to the hydrated salts. O. Boch's values for the sp. gr. of aq. soln. are indicated below.

According to W. P. Bloxam, the **melting point** of pentahydrated potassium sulphide is about 60°, and it loses only a trace of hydrogen sulphide if heated to 560°. J. Thomsen gives for the **heat of formation** (Li_2, S, aq) 115·22 Cals., and (Na_2, S, aq.), 52·0 Cals., E. Filhol and J. B. Senderens' value for (Na_2, S, aq.) is 51·6 Cals., and P. Sabatier's value is 51·6 Cals., (Na_2, S_{solid}), 44·1 Cals., and E. Filhol and J. B. Senderens, 44·2 Cals. P. Sabatier gives 97·52 Cals. for (K_2, S_{solid}), and (K_2, S_{gas}), 100·22 Cals. M. Berthelot gives $COS+2K_2O=K_2CO_3+K_2S+48·04$ Cals. J. Thomsen and P. Sabatier find that the heat of dilution for $Na_2S+120H_2O$ is insignificant, for, owing to hydrolysis, such a soln. contains the hydrosulphide, NaSH, not the monosulphide. The heat of the reaction, $NaOHaq+H_2S_{gas}$, varies with the conc. J. Thomsen gave $H_2Saq+2NaOHaq=7·802$ Cals.; KOHaq $+H_2Saq=KSHaq+7·7$ Cals.; and $KOHaq+KSHaq=K_2Saq-0$ Cals.—presumably the monosulphide does not exist in dil. soln., but in conc. soln. the thermal value increases with conc., *i.e.* as n decreases in K_2S+nH_2O, thus:

n . .	401	241	121	41	31	21	16	11	9
Q Cals. .	0	0·04	0·06	0·11	0·19	0·21	0·24	0·38	0·47

P. Sabatier gives for the **heat of hydration** with liquid water $Na_2S+4·5H_2O$, 10·0 Cals.; Na_2S+5H_2O, 10·8 Cals.; and Na_2S+9H_2O, 15·86 Cals. P. Sabatier gives 7·5 Cals. $Na_2S.4\frac{1}{2}H_2O+1\frac{1}{2}H_2O=0·8$ Cal., and for $Na_2S.5H_2O+4H_2O$, 5·06 Cals. Similarly, $K_2S+2H_2O=8·10$ Cals., $K_2S+5H_2O=19·75$ Cals., and $K_2S.2H_2O+3H_2O=11·65$ Cals. P. Sabatier gives 7·5 Cals. **heat of solution** of Na_2S at 14·5°; $Na_2S.5H_2O$, −3·3 Cals. at 77°; and $Na_2S.9H_2O$, −8·38 Cals. at 13°. P. A. Favre and J. T. Silbermann give 5·3 Cals. for the heat of soln. of K_2S, and P. Sabatier 5·0 Cals. for 500 parts of water at 18°, and for K_2S+2H_2O, 1·90 Cals. (16°); and K_2S+5H_2O, −2·60 Cals. (17°). P. Sabatier gives 9·9 Cals. for the heat of the reaction of hydrochloric acid with Na_2S, and 10·08 Cals. with $Na_2S.9H_2O$. The alkali sulphides are soluble in **water**; and, according to J. J. Berzelius, less soluble in **alcohol** than in water. The soln. are decomposed by acids with the evolution of hydrogen sulphide. A. Stromeyer found that even carbonic acid acts in this way. A. Braudrimont says that sodium sulphide is soluble in less than three-fourths of its weight of water; N. Parravano and M. Fornaini's measurements show the stable phases of sodium sulphide in aq. soln.

	10°	18°	28°	37°	45°	48°	50°	70°	90°
Per cent. Na_2S .	13·36	15·30	17·73	20·98	24·19	26·30	26·70	30·22	36·42
Solid phase . .			$Na_2S.9H_2O$				$Na_2S.6H_2O$		

The unstable phase $Na_2S.5\frac{1}{2}H_2O$ has a transition point, $Na_2S.9H_2O \rightleftharpoons Na_2S.5\frac{1}{2}H_2O + 3\frac{1}{2}H_2O$, at 49° when the soln. contains 29·3 per cent. Na_2S, and a transition point, $Na_2S.5\frac{1}{2}H_2O + \frac{1}{2}H_2O \rightleftharpoons Na_2S.6H_2O$, at 92° when the soln. has 38 per cent. Na_2S. The solubilities of the unstable hemihenahydrate at 40°, 60°, and 80° are respectively 29·92, 31·38, and 33·95 per cent. of Na_2S. The equilibrium curve is shown in Fig. 37. The alkali sulphides suffer hydrolysis in aq. soln.: $Li_2S + H_2O \rightleftharpoons LiOH + LiSH$, and in consequence of the low ionization constant of the alkali hydrosulphide, the soln. have an alkaline reaction, and they show an appreciable partial press. of hydrogen sulphide. The lowering of the f.p. of an N-soln. of sodium sulphide is given as 3·571° by F. W. Küster and E. Heberlein. They also find that a $\frac{1}{10}N$-sodium sulphide soln. is hydrolyzed 86·4 per cent. J. Knox, however, believes that the soln. is still more hydrolyzed than supposed by F. W. Küster and E. Heberlein; a diluted soln. of potassium sulphide is practically a mixture of eq. parts of sodium hydrosulphide and sodium hydroxide. This agrees with the observations of J. Thomsen on dil. soln. of potassium sulphide, and with the observations of A. Bauer, H. Rose, and H. Kolbe.

O. Bock's values for the sp. gr. at 18° (water at 4° unity) and the eq. conductivities λ (18°) of sodium sulphide are:

Na_2S per cent.	2·02	5·03	9·64	14·02	16·12	18·15
Sp. gr.	1·0212	1·0557	1·1102	1·1583	1·1810	1·2158
λ	115·7	97·2	73·7	56·7	46·0	38·7

The anomalous change in the eq. conductivity with conc. is associated with the marked hydrolysis which occurs. Similarly for potassium sulphide:

K_2S per cent.	3·18	9·93	15·06	24·64	29·97	47·26
Sp. gr.	1·0265	1·0829	1·1285	1·2186	1·2672	1·4596
λ	139·7	120·3	108·2	80·8	66·2	2·06

The temp. coeff. of the conductivities were also determined. F. W. Küster found that if a fairly conc. soln. of disodium sulphide is electrolyzed between platinum electrodes with an e.m.f. of about 2 volts, yellow films due to the formation of polysulphide separate out in the liquid. After a time, sulphur suddenly appears on the surface of the anode, and then rapidly increases in thickness. The e.m.f. rises as the thickness of the sulphur increases, until at a certain stage the sulphur film suddenly breaks away; the e.m.f. now falls, and the phenomena recur in the same order. This periodicity is similar to that observed by W. Ostwald during the soln. of chromium in hydrochloric acid. Apart from the condition of the anode and electrolyte, it is found that the e.m.f., and consequently the current strength, must have a certain magnitude before sulphur separates and the periodicity appears. On the other hand, the e.m.f. must not be too great or the deposit of sulphur remains permanently on the anode. The "critical e.m.f." depends on the chemical composition of the electrolyte, its conc., temp., and its stillness or otherwise. In soln. of sodium hydrosulphide, no periodic phenomena are observed. It is suggested that during electrolysis the sulphur liberated at first at the anode is taken up by the sulphur ions of the soln. to form polysulphide ions until saturation occurs; sulphur then separates, and the current becomes feeble owing to the resistance of the sulphur. During the time when the current is feeble, the polysulphide ions migrate away from the anode more quickly than they are formed, whilst the monosulphide ions (which can take up sulphur) migrate towards the anode and eventually break down the layer of sulphur.

W. P. Bloxam boiled a 20 per cent. soln. of pentahydrated potassium sulphide for $2\frac{1}{2}$ hrs. in contact with air; the evolution of hydrogen sulphide was negligibly small, and only traces of polysulphide and sulphite were formed, together with a little thiosulphate. Only a trace of hydrogen sulphide was evolved when the boiling was conducted for $1\frac{1}{2}$ hrs. in a stream of hydrogen gas. Contrary to the opinion of H. E. Schöne, the boiling soln. is fairly stable.[8] With dil. soln. hydrogen

sulphide is evolved, and thus potassium sulphide decomposes into potassium hydrosulphide and potassium hydroxide, also in vacuum or when hydrogen is passed through the soln.

Aq. soln. of sodium sulphide are oxidized in **air,** and sodium thiosulphate is formed. E. Mitscherlich says half the sodium sulphide is converted into thiosulphate, and half into carbonate. F. W. Durkee found that thiosulphate is first formed in the electrolysis of sodium sulphide soln. and finally sodium sulphate. A. Scheurer-Kestner and M. Merle did not confirm the intermediate formation of the thiosulphate. M. Trautz and K. T. Volkmann have also studied the reaction, and F. Thomas, the effect of different-coloured light. W. Gossage decomposed sodium sulphide into the hydroxide by **steam**: $Na_2S+2H_2O=2NaOH+H_2S$. J. Pedder recommended roasting the sulphide with carbon to convert it into carbonate, $2Na_2S+2C+5O_2=2Na_2CO_3+2SO_2$. When the soln. of sodium sulphide is oxidized with **potassium nitrate,** G. Lunge and P. Pauli found sodium thiosulphate is first formed, and at a higher temp. the sulphate. When oxidized with potassium permanganate, M. Hönig and E. Zatzek found that sulphur, sulphate, and trithionate are formed in the cold, only the sulphate is formed in hot soln. According to J. Kolb and R. Laming, when a soln. of sodium sulphide is treated with **ammonium carbonate,** sodium carbonate and ammonium hydrosulphide are formed; A. Stromeyer found that with **sodium hydrocarbonate**, hydrogen sulphide is evolved; J. Wilson, C. F. Werckshagen, and C. Böhringer and G. Clemm patented the process for converting the sulphide into carbonate. T. J. Pelouze, G. Clemm, and J. Kolb studied the action of **lime** and **magnesia.** T. du Motay recommended caustic lime for decomposing sodium sulphide. J. R. Wagner found that, with **aluminium hydroxide,** hydrogen sulphide is evolved and sodium aluminate is formed; W. H. Clayfield (1804) patented the use of lead or zinc oxides for converting sodium sulphide to the hydroxide. C. P. Prückner and L. Possoz recommended copper oxide. With **cuprous oxide,** sodium thiosulphate and copper oxide are formed; and, according to G. E. Habich, the reaction is faster with **ferric hydroxide,** and sulphur is precipitated. The use of ferric or manganic oxides in converting sodium sulphide to hydroxide was patented by J. Wilson (1838), W. Gossage (1859), and F. Ellershausen (1890). G. Lunge says that a soln. of sodium sulphide attacks **iron,** and the surface of the soln. is blackened on exposure to air. For the action of carbon dioxide on sodium sulphide, *vide* alkali carbonates.

According to A. Mourlot, lithium sulphide crystallized in the electric furnace is not attacked by **hydrogen** even at high temp.; **chlorine** and **bromine** attack it at ordinary temp.—bromine more slowly than chlorine—and **iodine** does not act below 200°. At 300° oxygen forms lithium sulphate. A. Mailfert found that **ozone** also converts the alkali sulphides to sulphates. **Phosphorus** does not act even at 1000°. In the electric oven lithium sulphide reacts with **carbon** to form the carbide. According to J. J. Berzelius, molten sodium sulphide attacks **glass** and becomes yellow. According to A. P. Dubrunfaut and A. Scheurer-Kestner, calcium sulphide and sodium carbonate are formed when the eq. of one mol. of sodium sulphide and one mol. of **calcium carbonate** are heated together. According to T. Weyl, sodium sulphide absorbs **ammonia** when they are put together in a sealed tube, an orange-coloured mass is formed and partly dissolved. When this mass is heated with water ammonium sulphide is formed. R. Abegg and H. Riesenfeld found the solubility of ammonia in soln. of sodium sulphide to be a linear function of the Na_2S-conc.; and they measured the ammonia press. of N-soln. of ammonia in sodium sulphide. With soln. containing 0·5, 1, and 1·5 mol. of sodium monosulphide, the respective press. of the ammonia were 15·18, 16·94, and 18·55 mm., when the press. of the ammonia in N-aq. soln. was 13·45 mm. According to W. P. Bloxam, potassium sulphide is stable at a low red heat and does not decompose when it is melted. P. Berthier stated that it is volatilized at high temp. When it is roasted in the air, potassium sulphide

burns very slowly, and, according to J. J. Berzelius and P. Berthier, covers itself with a layer of potassium sulphate. According to A. Baudrimont, when potassium sulphide is heated in the vapour of **phosphorus trichloride,** potassium chloride, and phosphorus trisulphide are formed; with **phosphorus penta-chloride,** potassium chloride, phosphorus thiochloride, and phosphorus sulphide are formed. Potassium sulphide forms double compounds with the electronegative metal sulphides.

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§ 22. The Alkali Polysulphides

The alkali monosulphides dissolve sulphur forming polysulphides. E. Filhol[1] did not get any polysulphides by heating a soln. of sodium sulphide with sulphur in a sealed tube. W. P. Bloxam found that warm sodium hydrosulphide soln. dissolved nearly the theoretical amount necessary for forming Na_2S_2, but on cooling a large proportion of the sulphur separated out again. According to P. Sabatier, a soln. of a mol. of sodium sulphide in 18 of water dissolves sulphur corresponding with $Na_2+S_{4 \cdot 6}$: and H. C. Jones, by the action of metallic sodium on melted sulphur, obtained $Na_2+S_{3 \cdot 34}$, and he proved that free sulphur was present in the latter. F. W. Küster and E. Heberlein measured the solubility of sulphur in aq. soln. of sodium monosulphide. They found the solubility to be almost independent of the temp., although between the limits of 0° and 50°, the solubility did diminish very slightly with increase of temp. The solubility of sulphur in a soln. of sodium sulphide depends greatly on the dilution of the latter. It is greatest in a $\frac{1}{16}N$-soln., where the constitution of the soln. approximates to the formula $Na_2+S_{5 \cdot 24}$. There is evidence that in the soln. examined no uniform compounds are present, but that various substances are in a condition of complex equilibrium with one another. All sulphides and polysulphides undergo much hydrolysis in aq. soln. The extent of hydrolysis diminishes regularly with increasing amount of sulphur in the soln. It was also found that in aq. soln. the tetrasulphide, Na_2S_4, is marked by a peculiar stability, an observation confirmed by the work of A. Rule and J. S. Thomas. P. Sabatier also prepared several polysulphides by boiling sulphur with soln. of sodium monosulphide. Alcoholic soln. of sodium monosulphide were likewise found by H. Böttger to dissolve sulphur and form di-, tri-, tetra-, and penta-sulphides; but W. P. Bloxam was not able to confirm R. Böttger's results. A. Rule and J. S. Thomas found an alcoholic soln. of sodium hydrosulphide reacts readily with sulphur, giving off hydrogen sulphide and forms polysulphides. According to W. P. Bloxam, the highest product obtained by dissolving sulphur in a soln. of potassium hydrosulphide is K_4+S_9, although hot soln. can take up enough for K_2+S_5. According to W. Spring and J. Demarteau, the solubility S of sulphur in soln. of potassium monosulphide increases with temp. θ according to the relation: $S=S_0(1+0{\cdot}000950\theta+0{\cdot}000001930\theta^2)$, where S_0 represents the solubility at 0°. From the way the dissolved sulphur behaves towards mercury, ethyl iodide, etc., H. Böttger and F. A. Geuther think that the product should be regarded as a simple soln. of sulphur in the normal sulphide.

J. S. Thomas and A. Rule measured the f.p. of mixtures of sulphur and sodium or potassium sulphide; and W. Biltz and E. Wilke-Dörfurt measured the m.p. of

mixtures of sulphur with cæsium or rubidium. The combined results are indicated in Table XXXV and graphed separately in the curves, Figs. 38 to 41. Commenting on these results, J. S. Thomas and A. Rule say :

TABLE XXXV.—FREEZING AND MELTING POINTS OF SULPHUR AND THE ALKALI METALS.

Compound or Eutectic.	Sodium.	Potassium.	Rubidium.	Cæsium.
Disulphide . . .	445·0°	471·0°	420·0°	460·0°
Di-tri eutectic .	206·0	250·9	200·0	205·5°
Trisulphide . .	223·5°	252·0	213·0°	217·0°
Tri-tetra eutectic .	222·6°	? (amorphous)	148·5°	151·0°
Tetrasulphide . .	275·0	> 145·0°	> 160·0°	> 160·0°
Tetra-penta eutectic .	247·6	143·4°	159·5°	159·5°
Pentasulphide . . .	251·8	206·0°	231·0	210·0°
Penta-hexa eutectic .	—	182·9°	189·8°	178·0°
Hexasulphide . . .	—	189·0	201·0°	186·0°
Saturated solution .	249·6°	188·1	184·6°	172·8°

Whilst the polysulphides of potassium, rubidium, and cæsium resemble one another very closely, the sodium compounds exhibit notable differences. Thus, whilst the first-named three elements all form hexasulphides and stable pentasulphides, in the case of

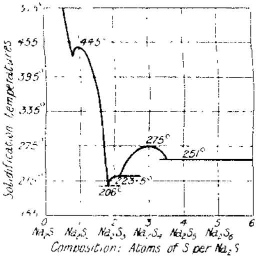

FIG. 38.—Freezing Point Curves of the Binary System $Na_2S - S$.

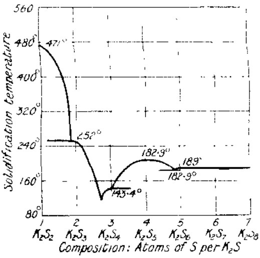

FIG. 39.—Freezing Point Curves of the Binary System $K_2S - S$.

sodium no trace of the existence of a hexasulphide could be detected, and the pentasulphide is relatively unstable. On the other hand, sodium tetrasulphide is stable and the trisulphide unstable, this order being reversed for the potassium, rubidium, and cæsium compounds. As regards their appearance, stability, and solidifying points, all the disulphides appear to be similar in character. Towards heat, these compounds show greater stability than any other of the polysulphides of the alkali metals. There is no evidence of the existence of intermediate compounds.

In attempting to prepare alkali polysulphides by the passage of hydrogen sulphide through an aq. soln. of the hydroxide in contact with an excess of finely powdered sulphur, the resulting soln. always contained polysulphide and thiosulphate—nor could the formation of the latter be avoided either by varying the conc. or the temp. Similarly also when sulphur is digested with soln. of the alkali hydroxides, both polysulphide and thiosulphate are formed. Soln. of the normal alkali sulphides, free from excess of hydrogen sulphide, hydrosulphide, or hydroxide give red polysulphide soln. when digested warm with sulphur. The soln. also contain thiosulphate, and it is therefore inferred that in spite of the failure of the ordinary tests to detect free alkali hydroxide, such must be present. Only when the sulphur is digested with a soln. of potassium or sodium hydrosulphide is the

product free from oxidized sulphur, to wit, thiosulphate. Hence, it is wrong to assume that it is a matter of indifference whether a soln. of the normal sulphide or the hydrosulphide be employed in preparing the sodium and potassium polysulphides. The older methods of preparing the polysulphides by digesting sulphur with the theoretical amount of alkali monosulphide in aq. soln., could not have yielded the desired polysulphide free from contamination with thiosulphate. Similarly, the dry methods of preparation—such as that employed by L. N. Vauquelin for making the lithium polysulphides, by melting lithium hydroxide with sulphur—do not yield a product free from oxidized sulphur—a carbonate is also frequently present. There is no known method of separating the polysulphide from the thiosulphate once the latter is formed. W. Biltz and E. Wilke-Dörfurt, however, did make definite polysulphides of rubidium and cæsium by the action of sulphur on the monosulphides. H. Böttger claimed to have made a series of alkali polysulphides by the action of sulphur on alcoholic soln. of the hydrated monosulphide, but W. P. Bloxam repeated the experiments and failed to confirm H. Böttger's results. A. Rule and J. S. Thomas prepared the polysulphides by dissolving sulphur in alcoholic soln. of the hydrosulphide.

Virtually nothing is known about the lithium polysulphides. Sodium tetrasulphide is the highest stable sodium polysulphide, although higher ones may be present in

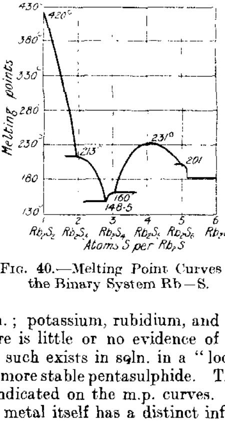

FIG. 40.—Melting Point Curves of the Binary System Rb—S.

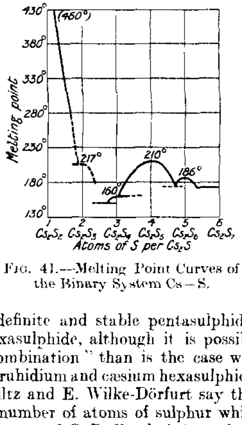

FIG. 41.—Melting Point Curves of the Binary System Cs—S.

soln.; potassium, rubidium, and cæsium form definite and stable pentasulphide; there is little or no evidence of potassium hexasulphide, although it is possible one such exists in soln. in a "looser state of combination" than is the case with the more stable pentasulphide. The existence of rubidium and cæsium hexasulphides is indicated on the m.p. curves. Hence, W. Biltz and E. Wilke-Dörfurt say that the metal itself has a distinct influence on the number of atoms of sulphur which can form a stable complex, and they apply R. Abegg and G. Bodländer's hypothesis to account for the formation of higher polysulphides of the alkali metals of higher mol. wt. According to this hypothesis, say A. Rule and J. S. Thomas, where the ionizing tendency imparted to the anion which may normally show a weak ionizing tendency, the anion, in order to "strengthen" itself, then tends to combine with other atoms or groups to form a complex. The ionizing tendency of the alkali metals increases with increase of at. wt., and in the case of the polysulphides, as the at. wt. of the metal increases there appears to be an increase in the number of sulphur atoms which go to make up the highest stable complex. H. J. Hamburger and R. Abegg, however, do not consider that the cation has a definite influence on the particular number of atoms taken up by the anion to form a complex, but only on the formation of complexes in general, the degree of the substance separating out depending on solubility conditions.

The alkali disulphides.—J. J. Berzelius [2] prepared crystals of **lithium disulphide,** Li_2S_2, by evaporating an aq. soln. of the hydrosulphide to a syrup and removing any carbonate which may be formed. The soln. furnished crystals of what J. J. Berzelius regarded as hydrated lithium disulphide. H. Böttger reported the formation of crystals of **pentahydrated sodium disulphide,** $Na_2S_2.5H_2O$, by cooling the dark-brown soln. obtained by digesting an alcoholic soln. of the corresponding monosulphide with the theoretical quantity of sulphur on a water-bath. The access of air to the soln. is, of course, prevented during these preparations. By working with a soln. containing a little extra sodium hydroxide, and cooling to $-10°$, golden-yellow crystals of **trihydrated sodium disulphide,** $Na_2S_2.3H_2O$, were obtained by H. Böttger. Attempts by W. P. Bloxam to prepare sodium disulphide by treating a soln. of the hydrosulphide with the calculated amount of sulphur under the influence of heat and in a current of hydrogen sulphide, were not successful. A. Rule and J. S. Price prepared anhydrous **sodium disulphide,** Na_2S_2, in the following manner :

A solution of 2 grms. of sulphur in 50 c.c. of absolute ethyl alcohol was sat. with hydrogen sulphide ; 4·17 grms. of sulphur were added, and the soln. was boiled on the water-bath for about one hour, a rapid current of hydrogen being passed through it. An excess of sodium (4 grms.) was added to the hot soln., and after boiling for a short time the bright yellow precipitate was collected, washed with absolute ethyl alcohol, and dried in a vacuum over phosphoric oxide. With lower proportions of sodium, the ratios of sodium to polysulphide sulphur were rather low—possibly owing to the formation of small quantities of tetrasulphide.

A. Rule and J. S. Price also noted that when metallic sodium is added to an alcoholic soln. of sodium tetrasulphide, there is an immediate separation of yellow crystals of the disulphide.

What were possibly very impure forms of **potassium disulphide,** K_2S_2, were reported by P. L. Geiger as a yellowish-red crystalline mass obtained by calcining two mols. of potassium hydrosulphate with over seven gram-atoms of carbon ; and by J. J. Berzelius, as the result of treating potassium carbonate with sulphur in a similar manner ; and as a result of exposing to air an alcoholic soln. of potassium hydrosulphide. So soon as the surface of Berzelius' liquid began to appear turbid, owing to the formation of thiosulphate, he evaporated the liquid to dryness in vacuo, and obtained what he regarded as potassium disulphide. W. P. Bloxam did not succeed in making this salt. A. Rule and J. S. Thomas mixed sulphur with an alcoholic soln. of sodium hydrosulphide, and after driving off some of the alcohol obtained a yellow solid, which, when dried in vacuo, was not homogeneous and contained some unchanged hydrosulphide ; likewise by adding dry ether to the same alcoholic soln. a white solid was obtained which contained alcohol along with sodium and sulphur in the 2 : 2 proportion. Similar results were obtained with the potassium salt, but very little disulphide is formed. A. Rule and J. S. Thomas found that there is a perceptible maximum in the f.p. curve of mixtures of potassium monosulphide and sulphur, corresponding with a m.p. at about 471°. W. S. Dumont has described a crystalline *alcoholated potassium disulphide,* $K_2S_2.C_2H_5OH$.

W. Biltz and E. Wilke-Dörfurt found that when rubidium pentasulphide is desulphurized by heating it in a current of hydrogen, the rate of evolution of sulphur becomes very slow at points corresponding with the disulphide, although the results are complicated by the volatility of the disulphide itself. When the residue, however, is dissolved in water, and evaporated, crystals of monohydrated **rubidium disulphide,** $Rb_2S_2.H_2O$—in one case crystals of $Rb_2S_2.2\,3H_2O$—were obtained. The corresponding monohydrated **cæsium disulphide,** $Cs_2S_2.H_2O$, was obtained in an analogous manner. The anhydrous sulphides are obtained as just indicated by desulphurizing the pentasulphides in a stream of hydrogen, or dehydrating the salt which crystallizes from the aq. soln. Rubidium and cæsium disulphides have not been obtained by crystallization from the mixed soln. of sulphur and the monosulphides.

H. Böttger's pentahydrated sodium disulphide is described as forming sulphur-yellow radiating masses of crystals; P. L. Geiger's anhydrous potassium disulphide as a yellowish-red deliquescent mass; W. Biltz and E. Wilke-Dörfurt's anhydrous cæsium and rubidium disulphides as dark-red amorphous very deliquescent masses. The hydrated crystals of sodium disulphide, says H. Böttger, do not effloresce over conc. sulphuric acid, but at 45° they lose a portion of the water of crystallization, and at 100° they lose three-fifths of the combined water, and at the same time melt to a reddish-brown liquid. The **melting point** of sodium disulphide determined by J. S. Thomas and A. Rule is 445°, and of potassium disulphide, 471°; W. Biltz and E. Wilke-Dörfurt's value for rubidium disulphide is 420°, and for cæsium disulphide, 460°. The rubidium salt is also said to volatilize over 850°, and the cæsium salt over 800°. P. Sabatier gives for the **heat of formation** of sodium disulphide $(Na_2.S_{2solid})=Na_2S_2aq+104\cdot2$ Cals., and $Na_2Saq+S_{solid}=Na_2S_2aq+1\cdot4$ Cals. For the **heat of solution,** P. Sabatier also gives 17·95 Cals. at 12°. F. W. Küster and E. Heberlein find the **degree of hydrolysis** of a $\frac{1}{10}N$-soln. of sodium disulphide to be 64·6 per cent., and the **freezing point** of a N-soln. $-3\cdot016°$.

The alkali trisulphides.—According to H. E. Schöne,[3] when a mixture of sodium carbonate with an excess of sulphur is heated to dark redness in a stream of carbon dioxide, **sodium trisulphide,** Na_2S_3, mixed with the sulphate is formed; J. J. Berzelius used a similar process for making **potassium trisulphide,** K_2S_3. J. J. Berzelius also made the potassium salt by passing the vapour of carbon disulphide over heated potassium carbonate; potassium thiocarbonate, K_2CS_3, is formed as an intermediate product, and finally a mixture of carbon and potassium trisulphide remains. J. J. Berzelius also made the same salt by passing hydrogen sulphide over the heated sulphate. J. Locke and A. Austell claim to have obtained the same salt by warming metallic sodium with a soln. of the right proportion of sulphur in toluene or naphthalene. C. Hugot also reports that he made potassium trisulphide by treating sulphur with a soln. of potassium in liquid ammonia. The red soln. does not solidify at $-79°$, and it is difficult to separate the sulphide from sulphur because both are soluble in the liquid. H. Böttger poured 149 grms. of a 7·6 per cent. alcoholic soln. of sodium hydroxide into one of sodium monosulphide, and then added 14·3 grms. of sulphur. The mixture was warmed at 90° on a water-bath while excluded from contact with air. Masses of golden-yellow crystals of **trihydrated sodium trisulphide,** $Na_2S_3.3H_2O$, separated from the soln. when cooled to $-10°$.

In spite of these reports, it is really very doubtful if the trisulphides of potassium and sodium have been obtained except in an impure condition. W. P. Bloxam's attempts to make sodium trisulphide by dissolving the calculated amount of sulphur in a soln. of sodium hydrosulphide under the influence of heat, and during the passage of a stream of hydrogen sulphide were not successful. W. P. Bloxam digested a soln. of potassium hydrosulphide with sulphur in the proportions required for the disulphide, and conc. the soln. by passing hydrogen sulphide through the hot liquid. The resulting product approximated to potassium trisulphide, and therefore furnished a higher sulphide than corresponded with the added sulphur. When the proportion of sulphur employed corresponded with that required for the trisulphide, the product contained approximately K_4S_7, and was probably a mixture. A. Rule and J. S. Thomas mixed the required proportion of sulphur with an alcoholic soln. of sodium hydrosulphide and, on the addition of ether, obtained a viscid yellow precipitate which proved to be a mixture of the unchanged hydrosulphide with sulphur, and a portion of polysulphide. With the potassium salt, too, when the quantity of sulphur less than that required for the tetrasulphide is added to an alcoholic soln. of the hydrosulphide, very little di- or tri-sulphide is formed. A. Rule and J. S. Thomas found that the f.p. curves of sodium monosulphide and sulphur, Fig. 37, show a break in the curve corresponding with the formation of an unstable sodium trisulphide which decomposes below its m.p.

Similar remarks apply to the f.p. curve of mixtures of potassium monosulphide and sulphur.

W. Biltz and E. Wilke-Dörfurt made reddish-yellow anhydrous **rubidium trisulphide,** Rb_2S_3, by heating the pentasulphide in a current of nitrogen when the rate of evolution of sulphur becomes very slow at a point corresponding with the formation of the trisulphide, just as when heated in a stream of hydrogen, the slackening in the speed of desulphurization corresponds with the formation of the disulphide. If the product be dissolved in water and recrystallized, fairly pure monohydrated rubidium trisulphide, $Rb_2S_3.H_2O$, is formed in yellow lustrous leaflets. Similar remarks apply to the formation of anhydrous **cæsium trisulphide,** Cs_2S_3, and of yellow leaflets of monohydrated cæsium trisulphide, $Cs_2S_3.H_2O$. Both the anhydrous trisulphides of rubidium and cæsium show well-defined maxima on the fusion curves of the alkali metals and sulphur. The salts could not be *prepared in soln. by the action of sulphur on soln. of the monosulphide.*

J. J. Berzelius said anhydrous potassium trisulphide appears in yellowish-brown masses which, said H. E. Schöne, show the presence of prismatic crystals on a fractured surface. W. Biltz and E. Wilke-Dörfurt say the anhydrous cæsium trisulphides form reddish-yellow to brownish-yellow hygroscopic masses, while the monohydrates form yellow plates. A. Rule and J. S. Thomas give 223·5° for the **melting point** of sodium trisulphide, and 252·0° for the potassium salt, and H. E. Schöne says the molten potassium solid is stable at 900°. W. Biltz and E. Wilke-Dörfurt give 213° for the m.p. of the rubidium salt, and 217° for the cæsium salt. H. Böttger says that the crystals of trihydrated sodium trisulphide melt at 100° to a liver-brown liquid which loses two-thirds of its combined water; he adds that the crystals can be kept unchanged in air for a long time; and that they gradually effloresce even in closed vessels. J. J. Berzelius says that an aq. soln. of the potassium salt is brownish-yellow, and that the colour gradually disappears as potassium thiosulphate is formed, and sulphur precipitated. P. Sabatier found the **heat of formation** of sodium trisulphide $(Na_2.S_{3\,solid})=Na_2S_3aq+106·4$ Cals.; $Na_2S_2aq+S_{2\,solid}=3·2$ Cals.; and the **heat of solution** per gram eq. at 12° is 17·0 Cals. F. W. Küster and E. Heberlein find the **degree of hydrolysis** of a $\frac{1}{10}N$-soln. of sodium trisulphide to be 37·6 per cent and the **freezing point** of an N-soln. −2·688°.

The alkali tetrasulphides.—L. N. Vauquelin [4] melted sodium carbonate with the calculated amount of sulphur for the ratio Na : S=1 : 2, and extracted from the pulverized cake as much sodium sulphate as possible by digestion with absolute alcohol. P. Sabatier made the same compound by heating sodium monosulphide with the calculated amount of sulphur in an atm. of dry hydrogen. The residue was assumed to be anhydrous **sodium tetrasulphide,** Na_2S_4. J. J. Berzelius made **potassium tetrasulphide,** K_2S_4, by the action of carbon disulphide vapour on the heated sulphate. H. E. Schöne made *hexahydrated sodium tetrasulphide,* $Na_2S_4.6H_2O$, by boiling a soln. of a lower sulphide with an excess of sulphur for a short time, and evaporating the soln. to a syrup in vacuo. The mixture when treated with alcohol and allowed to stand in a cool place furnished pale yellow plates. These were washed with alcohol and ether, and preserved under ether. The salt is said by H. E. Schöne to give *trihydrated sodium tetrasulphide,* $Na_2S_4.3H_2O$, when heated between 100° and 120°. H. Böttger claimed to have made *octohydrated sodium tetrasulphide,* $Na_2S_4.8H_2O$, by digesting an alcoholic soln. of sodium hydroxide with sulphur on a water-bath. The pale red liquid if sufficiently conc. gives orange-red crystalline masses when cooled to −15°. H. E. Schöne obtained *trihydrated potassium tetrasulphide,* $K_2S_4.3H_2O$, by a method analogous to that employed for the hexahydrated sodium salt; and *hemihydrated potassium tetrasulphide,* $K_2S_4.\frac{1}{2}H_2O$, is formed on exposure in vacuo over sulphuric acid. H. E. Schöne also precipitated a yellow oil by adding 80 per cent. alcohol to aq. soln. of potassium tetra- or penta-sulphide. Absolute alcohol extracts water from the oil and causes it to crystallize. The analyses of the crystals agree with *dihydrated potassium tetrasulphide,* $K_2S_4.2H_2O$,

and of the oil with *octohydrated potassium tetrasulphide*, $K_2S_4.8H_2O$. There are serious doubts whether any of the alkali tetrasulphides here indicated are really chemical individuals.

W. P. Bloxam did not succeed in his attempts to make sodium tetrasulphide by dissolving the calculated amounts of sulphur in soln. of sodium hydrosulphide under the influence of heat, and during the passage of current of hydrogen sulphide. W. P. Bloxam also heated a soln. of potassium hydrosulphide with sulphur in the proportions to form K_2S_5, and found the sulphur dissolved on heating and deposited again on cooling. The soln. contained K : S in the proportions 4 : 9, and gave crystals of $K_4S_9.nH_2O$, which, when extracted with carbon disulphide, gave mustard-yellow tetrapotassium pentasulphide, $K_4S_5.10H_2O$; similar results were obtained with an excess of sulphur. With sulphur in the proportions for K_4S_5, only 50 per cent. of the hydrosulphide was active, and the product K_2S_4 yielded K_4S_5 on treatment with carbon disulphide. If the soln. of potassium hydrosulphide, with sulphur in the proportions required for K_2S_3 be conc. in a stream of hydrogen sulphide, crystals of $K_2S_4.3H_2O$ are obtained, and on recrystallization from alcohol, $K_2S.9\frac{1}{4}H_2O$. These results make it doubtful if W. P. Bloxam isolated a potassium polysulphide of undoubted individuality, but when the sulphur is added to the soln. within certain limits, the polysulphide obtained is richer in sulphur than corresponded with the sulphur added. This is interpreted to mean that *there is a tendency for the formation of one predominating sulphide, which in the case of potassium is the pentasulphide, and in the case of sodium is probably the tetrasulphide.*

By adding sulphur in the proportion required for the tetrasulphide to an alcoholic soln. of sodium tetrasulphide, A. Rule and J. S. Thomas obtained a deep-red soln., which, after boiling for an hour in a stream of hydrogen, and evaporating off most of the alcohol, furnished dark yellow crystals of anhydrous sodium tetrasulphide. When the experiments were repeated with the potassium salt, crystals of the pentasulphide were obtained, and the amount of hydrosulphide remaining unchanged decreased progressively with increasing amounts of sulphur. As previously indicated, when the proportion of sulphur is less than corresponds with the tetrasulphide, very little di- and tri-sulphides are formed; and with the value of the sulphur above the pentasulphide stage there is no indication of the formation of higher polysulphides than the pentasulphide. Assuming the reaction is: $2KSH + nS = K_2S_{n+1} + H_2S$, the amount of unchanged hydrosulphide in the soln. can be determined from the volume of hydrogen sulphide evolved. It was thus shown that the chief product of the action of sulphur on potassium hydrosulphide is the pentasulphide, and it is impossible to obtain the lower polysulphides by adding an eq. quantity of sulphur to soln. of the hydrosulphide. Similar remarks apply to sodium polysulphides, excepting that the stable salt is sodium tetrasulphide, and small quantities of higher sulphides are probably present in the soln. when the conc. of the sulphur is high, but decompose: $Na_2S_5 \rightarrow Na_2S_4 + S$ as evaporation proceeds.

A. Rule and J. S. Thomas found a well-defined maximum in the f.p. curve of mixtures of sodium monosulphide and sulphur, corresponding with the formation of stable sodium tetrasulphide, Fig. 38; but with the potassium monosulphide-sulphur curve, Fig. 39, potassum tetrasulphide appears as an unstable salt decomposing below its m.p. Similar remarks apply to W. Biltz and E. Wilke-Dörfurt's f.p. curve of rubidium and sulphur, Fig. 40, and of cæsium and sulphur, Fig. 41. Both the rubidium and cæsium tetrasulphides appear at their m.p. as unstable compounds. Small yellow crystals of dihydrated **rubidium tetrasulphide**, $Rb_2S_4.2H_2O$, were obtained from an aq. soln. of the monosulphide containing the theoretical amount of sulphur; and reddish-yellow prisms of anhydrous **cæsium tetrasulphide**, Cs_2S_4, were prepared in an analogous manner. No other sulphides of uniform composition could be isolated from the monosulphide soln. containing variable amounts of sulphur.

According to A. Rule and J. S. Price, anhydrous sodium tetrasulphide is a

dark-yellow crystalline solid with an olive-green tinge; the **crystals,** suspended in a xylene soln. of Canada balsam, are perfect cubes. According to P. Sabatier, sodium tetrasulphide forms a red hygroscopic brittle mass; H. E. Schöne also describes the potassium salt as a reddish-brown crystalline mass; while W. Biltz and E. Wilke-Dörfurt say the rubidium and cæsium salts are reddish-yellow masses. H. E. Schöne says hexahydrated sodium tetrasulphide forms hygroscopic pale-yellow crystalline plates; H. Böttger describes octohydrated sodium tetrasulphide as forming an orange-red crystalline mass; H. E. Schöne says that trihydrated potassium tetrasulphide forms orange-red plates; and the hemihydrated salt yellow crystals. Dihydrated rubidium sulphide forms pale yellow prisms.

A. Rule and J. S. Thomas say the **melting point** of sodium tetrasulphide is 275°, and of the potassium salt over 145°. When the sodium salt is heated in a capillary tube, it becomes orange-red at 115°–120°, begins to sinter at about 258°, and forms a dark-red liquid at about 267°. H. E. Schöne says that anhydrous potassium tetrasulphide is stable at about 800°, but gives off sulphur at a higher temp., and forms the trisulphide. P. Sabatier says that sodium tetrasulphide is very readily oxidized in air, for it is soon covered by a film of sulphur and sodium thiosulphate. W. Biltz and E. Wilke-Dörfurt say that each of the rubidium and cæsium salts melts above 160°. H. E. Schöne says that hexahydrated sodium tetrasulphide melts at 25°, forming a dark-red syrupy liquid which when heated to 100°–120° loses two-thirds of its water, and the resulting $Na_2S_4.2H_2O$ then melts at a still higher temp.; this salt decomposes when heated to redness, water and sulphur are given off, and the cold residue of a yellowish-red colour contains polysulphides and a thiosulphate. H. Böttger's octohydrated sodium tetrasulphide effloresces over conc. sulphuric acid, and loses a part of its water at 40°, but no sulphur is lost at 100°, although hydrogen sulphide is evolved at higher temp. H. E. Schöne's trihydrated potassium tetrasulphide is said to melt when heated in a glass tube, and water, hydrogen sulphide, and sulphur are given off. The hot molten product is dark brown when hot, and much paler when cold. P. Sabatier gives the **heat of formation** (Na_2,S_{4solid}) $=98.4$ Cals.; $(Na_2,S_{4solid})=Na_2S_4aq+108.2$ Cals.; $(Na_2S.S_{3solid})=10.2$ Cals.; $(Na_2Saq,S_{3solid})=Na_2S_4aq+5$ Cals. P. Sabatier also gives $(K_2,S_{solid})_4=116.6$ Cals.; $(K_2,S_{4solid})=K_2S_4aq+117.8$ Cals.; $(K_2S,S_{3solid})=K_2S_4aq+5.2$ Cals.; $(K_2S,S_3)=12.4$ Cals.; $K_2S_4+\frac{1}{2}H_2O=2.66$ Cals.; $K_2S_4+2H_2O=5.76$ Cals.; and $K_2S_4.\frac{1}{2}H_2O+1\frac{1}{2}H_2O=3.1$ Cals. P. Sabatier also gives 16·1 Cals. for the **heat of solution** of sodium tetrasulphide at 12°, and 4·9 Cals. for the heat of formation in 600 mols. of water at 16·5°. E. Filhol and J. B. Senderens' determinations are in agreement with P. Sabatier's. P. Sabatier gives 3·74 Cals. for the heat of soln. of $K_2S_4.2H_2O$. F. W. Küster and E. Heberlein find the **degree of hydrolysis** of an aq. soln. of sodium tetrasulphide to be 11·8 per cent., and the **freezing point** of an N-soln. $-2.421°$.

The sodium salt is very hygroscopic, and the hygroscopicity appears to increase in passing from potassium to cæsium tetrasulphide. The tetrasulphides are readily soluble in water; the sodium salt forms a clear deep orange soln. which becomes dark red when heated; if exposed to air, the aq. soln. soon begins to deposit sulphur. Alcoholic soln. behave similarly, and they are even more liable to oxidation by exposure to air. An excess of ether precipitates a red oil from the conc. alcoholic soln., and this forms a viscid, yellow crystalline solid when continuously stirred. The precipitate is probably a definite alcoholate; most of the alcohol can be removed in vacuo over phosphorus pentoxide. Alcohol adheres to this solid very tenaciously, and if attempts be made to remove the last traces of alcohol by heating the salt in a stream of hydrogen a little sulphur is lost. A. Rule and J. S. Thomas found that pyridine is coloured an intense green in contact with sodium tetrasulphide, and the solid slowly changes in colour to bright yellow—possibly a complex is formed.

The alkali pentasulphides.—J. J. Berzelius[5] prepared **potassium pentasulphide,** K_2S_5, by heating potassium, or one of the lower sulphides with an excess of sulphur,

until the excess vaporized. H. E. Schöne added that the temp. should not exceed 600°. M. J. Fordos and A. Gélis say that at 105° a mixture of the monosulphide and thiosulphate is formed, and at the higher temp. the latter is decomposed into pentasulphide and sulphate: $4K_2S_2O_3=3K_2SO_4+K_2S_5$. E. Drechsel also made anhydrous potassium pentasulphide by first heating potassium carbonate in a stream of hydrogen sulphide, then mixing the product with sulphur, and again heating the mixture in a stream of the same gas as before. J. J. Berzelius heated four mols. of potassium hydroxide or carbonate with at least 16 gram-atoms of sulphur. The reaction with the hydroxide was stated to be $6KOH+12S=2K_2S_5+K_2S_2O_3+3H_2O$. E. Mitscherlich says that during the reaction: $4K_2CO_3+16S=3K_2S_5+K_2SO_4+4CO_2$, the mixture is very apt to swell inconveniently if it contains moisture. The excess of sulphur, however great, can be volatilized, but if the temp. be not high enough, the excess of sulphur floats as a separate stratum on the top of the alkali pentasulphide. If the temp. does not exceed 250°, all the carbon dioxide will be expelled, and a mixture of pentasulphide and thiosulphate remains. Potassium pentasulphide is soluble in alcohol, the thiosulphate is not soluble, and the obvious method of purification has been employed, but W. P. Bloxam showed that the separation is not so effective because, in the presence of the pentasulphide, some thiosulphate dissolves.

The dry methods of preparation give but a crude product; equally unsatisfactory are the older wet processes. J. J. Berzelius prepared an aq. soln. of potassium pentasulphide by digesting one of the lower sulphides, or hydrosulphide with sulphur until sat.; with the hydrosulphide hydrogen sulphide is evolved as sulphur dissolves. H. E. Schöne says the action takes place slowly in the cold—about 3 weeks. Some thiosulphate is also formed. H. Rose boiled sulphur with a soln. of potassium carbonate, and obtained a mixture of the pentasulphide and thiosulphate; similar results were obtained with potassium hydroxide. H. E. Schöne prepared hexahydrated **sodium pentasulphide,** $Na_2S_5.6H_2O$—possibly mixed with the corresponding tetrasulphide—by dissolving sulphur in the monosulphide, evaporating the soln. to a syrup, and adding alcohol. He suggests that the product is possibly a mixture of the tetrasulphide with sulphur. H. Böttger dissolved the necessary amount of sulphur in a soln. of the monosulphide, and, after exposure for some days to a winter's cold, obtained crystals of the tetrasulphide; the mother liquid, at −5°, gave dark orange-yellow crystals of octohydrated sodium pentasulphide, $K_2S_5.8H_2O$. E. Drechsel also prepared the pentasulphide by boiling an alcoholic soln. of the hydrosulphide with pentasulphide, $2KSH+H_2S_5=K_2S_5+2H_2S$; and C. Hugot made impure sodium pentasulphide by dissolving an excess of sulphur in a soln. of sodium in liquid ammonia. The red soln. does not solidify at −79°; the residue left on evaporating the ammonia contains some admixed sulphur which is soluble in the liquid.

W. P. Bloxam did not succeed in making sodium pentasulphide by the action of the calculated amount of sulphur on the hydrosulphide under the influence of heat, and during the passage of a current of hydrogen sulphide. This is confirmed by the work of A. Rule and J. S. Thomas, who tried to make sodium pentasulphide by dissolving the calculated amount of sulphur in alcoholic soln. of the hydrosulphide, but found that while a pure sodium tetrasulphide can be obtained when Na : S=2 : 4 in the soln., the products with a smaller proportion of sulphur are probably mixtures of tetrasulphide with unchanged hydrosulphide, and a larger proportion of sulphur the product was heterogeneous. In W. P. Bloxam's attempt to make potassium pentasulphide by dissolving the requisite amount of sulphur in a hot aq. soln. of the monosulphide, aided by heat, and concentrating the soln. in a stream of hydrogen sulphide, he found that the hot soln. takes up enough sulphur to form the pentasulphide, but some is deposited on cooling, to form a stable soln. containing K : S in the ratio 4 : 9, but if the hot soln. is conc. in a stream of hydrogen sulphide, a soln. is obtained which furnishes crystals of the hydrated potassium pentasulphide, $K_2S_5.nH_2O$. W. P. Bloxam accounted for the

formation of a higher polysulphide than can be obtained by the direct soln. of sulphur in the hydrosulphide as follows :

Hydrogen sulphide rapidly decomposes polysulphides, if passed through a *cold* soln., sulphur being copiously deposited and potassium hydrosulphide formed. If, however, hydrogen sulphide is passed through a *hot* soln. of a polysulphide, no deposition of sulphur is observed, but the depth of colour is increased. It is suggested that some potassium hydrosulphide is formed on passage of hydrogen sulphide through a *hot* soln. of K_4S_9, and that the liberated sulphur, at the moment of its separation, is taken up by unaltered K_4S_9, forming the higher compound K_4S_{10}.

W. P. Bloxam's product, K_4S_{10} or K_2S_5 may be a mixture, since it appears as the end-member of a series of products, K_4S_5, K_4S_6, K_4S_7, K_4S_8, K_4S_9, and K_4S_{10}, many or all of which are probably mixtures of a polysulphide with the hydrosulphide. Just as sodium tetrasulphide is probably the most stable polysulphide of sodium, so potassium pentasulphide is probably the stable polysulphide of potassium. Consequently, the end-term of Bloxam's series is probably a true pentasulphide. A. Rule and J. S. Thomas prepared highly satisfactory potassium pentasulphide by the following process :

One gram of potassium was dissolved in 15 c.c. of absolute ethyl alcohol, and the soln. was sat. with dry hydrogen sulphide. 1·64 grms. of finely ground recrystallized rhombic sulphur were added, and the soln. was boiled gently on a water-bath for about one hour, a rapid current of dry hydrogen being passed through it. On the addition of the sulphur a vigorous reaction at once took place even in the cold with evolution of hydrogen sulphide, and the soln. became deep red. The sulphur dissolved, and after a short time a bright orange-red crystalline solid separated out. The soln. was conc. to about 5 c.c., the product collected on a filter, sprayed with alcohol, and kept in a vacuum over phosphoric oxide.

A. Rule and J. S. Thomas' f.p. curves of binary mixtures of sodium and potassium monosulphides with sulphur—Figs. 36 and 39—show that while potassium pentasulphide gives a well-defined maximum, the maximum with sodium pentasulphide is very much flattened. R. Kremann has shown that the dissociation of a compound must be attended by the flattening of the maximum on the freezing or fusion point curve, and this the more the greater the extent of the dissociation. Hence, it is evident that sodium pentasulphide must be very much dissociated because of the very slight rise of the maximum. Similar results were obtained by R. Abegg and A. Hamburger with certain potassium polyiodides. The well-defined maximum observed by W. Biltz and E. Wilke-Dörfurt in the fusion-point curve of mixtures of rubidium sulphide and sulphur shows the existence of a stable **rubidium pentasulphide**, Rb_2S_5, a dark-red crystalline solid which was prepared by melting together one of the lower sulphides with the requisite amount of sulphur, and also by the action of warm soln. of the monosulphide on powdered sulphur and aq. alkali hydroxide in an atmosphere of hydrogen. Similar remarks apply to **cæsium pentasulphide**, Cs_2S_5, which also shows a well-defined maximum on the fusion curve of binary mixtures of cæsium and sulphur and which is obtained in an analogous manner.

The hydrated sodium pentasulphides reported respectively by H. E. Schöne and H. Böttger are said to form brown or dark orange-yellow **crystals** ; these products are probably mixtures of sulphur and sodium tetrasulphide. Anhydrous potassium pentasulphide, prepared by the dry process, is said to be a dark yellowish-brown solid, and the specimen prepared by A. Rule and J. S. Thomas' process is described as forming glistening orange-red crystals. W. Biltz and E. Wilke-Dörfurt's rubidium pentasulphide is said to crystallize in dark-red rhombic prisms ; and the cæsium salt to form red crystals. Potassium pentasulphide is extremely hygroscopic and is rapidly oxidized on exposure to air with the liberation of sulphur ; the rubidium salt also deliquesces to a red liquid from which sulphur crystallizes out ; while the cæsium salt is not hygroscopic.

A. Rule and J. S. Thomas give 251·8° for the **melting point** of sodium pentasulphide, and 206° for that of the potassium salt. When the potassium salt is

heated in a capillary tube, it begins to darken at 130°, and appears quite black at 182°; it begins to sinter at 200°–205°, and melts not very sharply at about 220°. On cooling, the salt passes through similar colour changes in the reverse order, and finally assumes its original appearance; there are no signs of any decomposition, so that the salt can therefore be fused without decomposition. H. C. Jones says that when sodium pentasulphide is heated it gives off sulphur and forms the tetrasulphide. W. Biltz and E. Wilke-Dörfurt give 231° for the m.p. of rubidium pentasulphide salt, and 210° for that of the cæsium salt. H. Böttger says that the crystals of octohydrated sodium pentasulphide which he obtained lose part of their sulphur when heated to 100° in a stream of hydrogen, and at higher temp. liberated hydrogen sulphide. E. Drechsel says that potassium pentasulphide burns when heated in air, and it oxidizes to potassium sulphate and sulphur dioxide, and when oxidized slowly in badly stoppered vessels, it forms the thiosulphate and sulphur; when melted in a stream of water vapour, it forms potassium sulphate and hydrogen sulphide.

The alleged sodium pentasulphide was stated to dissolve in **water,** and H. C. Jones said that when the aq. soln. is warmed, hydrogen sulphide is evolved, forming the thiosulphate: $Na_2S_5+3H_2O=3H_2S+Na_2S_2O_3$. F. W. Küster and E. Heberlein give for the degree of hydrolysis of a soln., with the conc. of sulphur corresponding with $Na_2+S_{5\cdot24}$, to be 5·7 per cent. H. Buff reported that the conc. soln. of sodium pentasulphide is a good conductor of electricity—sulphur accumulates about the anode, sodium is discharged at the cathode, and the liquid is at the same time decolorized, forming sodium monosulphide. When the soln. is decolorized, hydrogen and oxygen are liberated at the electrodes, and some hydrogen sulphide is formed. A. Rule and J. S. Thomas found potassium pentasulphide dissolves readily in water, forming a red soln. which darkens in colour when heated. According to J. J. Berzelius, the aq. soln. of potassium pentasulphide has an alkaline bitter taste, and an alkaline reaction. According to H. Rose, the temp. falls as potassium pentasulphide dissolves in water. The aq. soln. deposits sulphur when exposed to air and forms thiosulphate: $2K_2S_5+3O_2=2K_2S_2O_3+6S$. W. Biltz and E. Wilke-Dörfurt say that rubidium pentasulphide is at once decomposed by water while the cæsium salt is unaffected. Potassium pentasulphide readily dissolves in **alcohol,** but less readily than in water, forming a red soln. which darkens in colour when warmed; if the salt be contaminated with potassium sulphate or thiosulphate most of these impurities remain undissolved. According to H. E. Schöne, 90 per cent. alcohol precipitates a red oil from conc. aq. soln., and this oil is thought to be the octohydrated tetrasulphide, $K_2S_4.8H_2O$. According to A. Rule and J. S. Thomas, the alcoholic soln. deposits sulphur when exposed to air; but, according to H. C. Jones, alcoholic soln. deposit sodium thiosulphate alone, and aq. soln. deposit sulphur alone. According to A. Rule and J. S. Thomas, if potassium pentasulphide be shaken with cold alcohol, a well-defined bright yellow alcoholate is formed in small monoclinic prisms. W. Biltz and E. Wilke-Dörfurt say that rubidium pentasulphide remains unchanged under cold alcohol, hot ethyl sulphide, or chloroform; and that the cæsium salt can be crystallized unchanged from 70 per cent. alcohol. The majority of organic solvents are without action on potassium pentasulphide. **Pyridine** in contact with potassium pentasulphide is coloured an intense brownish-red and the liquid becomes opaque—possibly a complex is formed; and **nitrobenzene** in contact with potassium pentasulphide is coloured magenta in the cold; the colour fades when warmed, and the salt can be fused below the liquid. The colour returns, and the salt remains unchanged. The red crystals of rubidium pentasulphide behave similarly in contact with nitrobenzene; and they are coloured yellow in contact with **carbon disulphide,** and the latter is slowly absorbed by the salt.

H. Böttger has said that when a soln. of the alleged sodium pentasulphide is boiled with **lead hydroxide,** it behaves like a mixture of sulphur and sodium monosulphide, for lead sulphide and sodium thiosulphate are produced; he adds that in

the first stage of the reaction lead sulphide, sodium hydroxide, and sulphur are produced, and that the two latter then react to form the thiosulphate. When an **acid** is gradually added to an aq. soln. of potassium pentasulphide, hydrogen sulphide, milk of sulphur, and the potassium salt of the acid are formed ; on the contrary, if the sulphide be gradually added to an excess of the acid, a potassium salt of the acid and hydrogen persulphide, H_2S_5, are formed. The lower sulphides behave in an analogous manner. According to A. Duflos, if **hydrogen sulphide** be passed into a soln. of the pentasulphide, sulphur is precipitated, and potassium sulphide is formed—hence, the affinities are reversed according to the temp. L. N. Vauquelin found that the aq. soln. of the pentasulphide readily gives up four-fifths of its sulphur to many of the heavy **metals**—very rapidly to *copper*—forming the metal sulphide, sulphur, and the alkali monosulphide ; similar remarks apply to the action of *silver* on the dry salt at a red heat—silver sulphide and potassium monosulphide are formed. According to M. Berthelot, when any of the polysulphides are heated to redness in a stream of **carbon dioxide,** sulphur, and a mixture of carbon monoxide, oxysulphide, and sulphur dioxide are formed. W. Spring and J. Demarteau say that **iodine** precipitates sulphur from soln. of the polysulphides ; the sulphur dissolves in the remaining monosulphide, forming the tetrasulphide ; **potassium sulphite** reacts with all polysulphides, forming thiosulphate and monosulphide ; they **dialyse** uniformly and completely, and are not to be regarded as colloidal soln. ; and they give ethyl disulphide, $(C_2H_5)_2S_2$, when treated with **ethyl bromide** or **ethyl iodide.** Hence, say W. Spring and J. Demarteau, one sulphur atom in the polysulphides may be regarded as more firmly fixed in the mol. than the others, $M_2S.S_n$, when their behaviour with inorganic substances is considered, and with the alkyl halides behave as if they had the formula $M_2S_2.S_n$, *i.e.* as soln. of sulphur in the disulphides. F. W. Küster and E. Heberlein regard them as salts of complex thio-acids of the type $M_2S.S_n$, analogous to the complex iodide, $MI.I_n$. For the general discussion on the constitution of the polysulphide, *vide* hydrogen persulphides.

The alkali hexasulphides.—A. Rule and J. S. Thomas' f.p. curve of mixtures of sulphur and sodium monosulphide, Fig. 38, immediately beyond the pentasulphide, becomes horizontal, corresponding with the formation of a sat. soln. of sulphur in sodium pentasulphide, melting at 249° ; and indicating that the pentasulphide is probably the highest polysulphide which can be obtained by fusing together sodium monosulphide and sulphur. With the f.p. curve of potassium monosulphide and sulphur, there is a much-flattened maximum corresponding with **potassium hexasulphide,** K_2S_6, showing that this compound is considerably dissociated at the m.p.—about 189°. With more than 7·5 per cent. of sulphur the curve becomes horizontal, and with still more sulphur, the mass separates into two layers—a sat. soln. of sulphur in the hexasulphide melting at 188°, and the other is virtually sulphur melting at 117·5°. W. Biltz and E. Wilke-Dörfurt's f.p. curve, Fig. 40, of mixtures of sulphur with rubidium, show that dissociated **rubidium hexasulphide,** Rb_2S_6, is formed, and this compound has been obtained as a brownish-red solid by melting together the requisite amount of sulphur with one of the lower sulphides. It melts at 201°, and with more sulphur the horizontal curve has a constant f.p. at 186·6°, the value for a sat. soln. of sulphur in molten hexasulphide. Brownish-red **cæsium hexasulphide,** Cs_2S_6, was obtained in a similar manner. The f.p. curve, Fig. 41, likewise shows that it is a dissociating solid melting at 186° ; that no higher sulphides are formed ; and the subsequent course of the curve has the constant m.p. of 172·8°—the value for a sat. soln. of sulphur in molten hexasulphide.

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§ 23. The Alkali Hydrosulphides

The preparation of the alkali hydrosulphides.—J. J. Berzelius [1] prepared **lithium hydrosulphide**—presumably impure LiHS—by the action of hydrogen sulphide on red-hot lithium carbonate. J. L. Gay Lussac and L. J. Thénard made brown masses of sodium and potassium hydrosulphide, KSH, by heating the alkali metal in a current of hydrogen sulphide. The reaction $2K+2H_2S\rightarrow 2KSH+H_2$ recalls the action of the same metal on water, $2K+2H_2O\rightarrow 2KOH+H_2$. Consequently, the same amount of potassium which, with water, gives one volume of hydrogen gas, also gives one volume of the same gas when heated with two volumes of hydrogen sulphide. According to P. Sabatier, these products always contain polysulphides; with sodium, he obtained a mass of the composition Na_3S_2H, and he also made the same salt by saturating a soln. of lithium sulphide with hydrogen sulphide, and evaporating the product to a syrupy liquid which was dried in vacuo over anhydrous potassium carbonate. He also gave an analogous process for making potassium hydrosulphide. J. J. Berzelius also made **sodium hydrosulphide,** NaSH, by the action of an excess of hydrogen sulphide on a soln. of sodium hydroxide. W. P. Bloxam sat. with hydrogen sulphide a 27·82 per cent. soln. of sodium hydroxide at 100°. W. Biltz and E. Wilke-Dörfurt obtained a soln. of **potassium hydrosulphide,** KSH, in a similar manner. H. E. Schöne recommended dehydrating the hydrated crystals by evaporating the soln. in vacuo or in a stream of hydrogen

sulphide, and subsequently dehydrating the crystals at 200°—W. P. Bloxam recommends 445°. C. Guéranger stated that crystals of the hydrosulphide cannot be obtained by evaporating the soln., because hydrogen sulphide is lost during the evaporation and the monosulphide, Na_2S, is formed. Hence, the soln. is conc. in an atm. of hydrogen sulphide. In P. Sabatier's method, crystals of enneahydrated sodium sulphide are sat. with hydrogen sulphide, and the soln. evaporated in a current of hydrogen sulphide free from air. According to W. P. Bloxam, the action is too slow; he failed to obtain the desired salt by this process. Instead, he recommended heating the crystals of the enneahydrate, $Na_2S.9H_2O$, to 85°, and saturating the fused salt with hydrogen sulphide, when the ratio Na : S in the soln. is that required for the hydrosulphide with but a slight deficiency—0·19 per cent.—of sulphur. The proportion of hydrogen sulphide absorbed depends on the conc. of the alkali hydroxide, for the more dil. the soln. the less the proportion absorbed. According to A. Rule, it is very doubtful if the alkali hydrosulphides of a high degree of purity have been made by wet processes.

W. P. Bloxam also described a method for making the anhydrous alkali hydrosulphides employed by A. Scott for the preparation of anhydrous potassium hydrosulphide. In this process, hydrogen sulphide is passed into rectified ether containing the alkali metal. With potassium, hydrogen is rapidly evolved from the surface of the metal which remains quite bright throughout the reaction, and potassium hydrosulphide separates as a snow-white powder. The product is washed with rectified ether, and on drying over sulphuric acid, in vacuo, it is obtained as a pale yellow, pulverulent crystalline mass. A. Rule prepared anhydrous potassium and sodium hydrosulphides in a high degree of purity by the action of hydrogen sulphide on the alkali ethoxide.

Two grams of sodium were dissolved in absolute alcohol, freshly distilled over quicklime, in a flask fitted with a reflux condenser. As sodium ethoxide began to separate out, more alcohol was added until just sufficient was present to retain the product in soln. at the room temp.—40 c.c. were needed. The flask was fitted with a 2-hole stopper fitted with delivery and egress tube to which calcium chloride tubes were attached. Hydrogen sulphide washed in water, and dried by a long column of calcium chloride was passed rapidly into the soln. A fine crystalline precipitate formed in the soln., and increased in amount with the continued passage of the gas. When the soln. was sat. with gas, the precipitate was collected, rapidly filtered, washed with absolute alcohol, and dried in vacuo over calcium chloride. The precipitate weighed 0·25 grm. When benzene or ether is added to the soln., a precipitate of pure anhydrous sodium hydrosulphide is obtained. This is washed and dried as before.

For preparing larger quantities of the hydrosulphide it is more convenient to carry out the reaction in the presence of an excess of the precipitant—say 5 grms. of sodium with a mixture of 10 grms. of absolute alcohol and 100 c.c. of pure dry benzene, more alcohol is added from time to time to keep the ethoxide in soln. until all the sodium is dissolved. This liquid is treated with hydrogen sulphide as before. The reaction seems to be quantitative and to be expressed by the equation: $C_2H_5ONa+H_2S=C_2H_5OH+NaHS$; potassium salt is prepared in a similar manner.

W. Biltz and E. Wilke-Dörfurt prepared **rubidium hydrosulphide,** RbSH, by the method used by J. J. Berzelius for lithium hydrosulphide; they also prepared **caesium hydrosulphide,** CsSH. Both salts crystallized in about a week from the aq. soln., in vacuo over calcium chloride, in white lustrous very deliquescent needle-like crystals of the anhydrous salts.

Two hydrated sodium hydrosulphides have been prepared. According to W. P. Bloxam, **dihydrated sodium hydrosulphide,** $NaHS.2H_2O$, is formed by evaporating the conc. soln. in a stream of hydrogen sulphide until crystals separate on rapid cooling; and also by evaporating a conc. soln. over sulphuric acid. R. Böttger regards this as *hemitrihydrated sodium hydrosulphide*, $NaSH.1\frac{1}{2}H_2O$. W. P. Bloxam says that **trihydrated sodium hydrosulphide,** $NaHS.3H_2O$, is formed in large colourless crystals when the dihydrate is allowed to stand for a long time

in the mother liquid. The same crystals were also prepared by A. Baudrimont. According to H. E. Schöne, the evaporation of a conc. soln. of the potassium salt in vacuo over calcium chloride and solid potassium hydroxide furnishes colourless transparent rhombohedral crystals of **tetartahydrated potassium hydrosulphide,** $KSH.\frac{1}{4}H_2O$; while W. P. Bloxam, and P. Sabatier obtained **hemihydrated potassium hydrosulphide,** $KSH.\frac{1}{2}H_2O$, under similar conditions. It is therefore not clear whether the salt is $4KSH.H_2O$ or $2KSH.H_2O$.

The properties of the alkali hydrosulphides.—According to A. Rule, the anhydrous alkali hydrosulphides form white, granular, pulverulent **crystals,** less pure forms are tinged yellow. The white colour often acquires a pale-yellow tinge during washing and drying. According to W. P. Bloxam, dihydrated sodium hydrosulphide forms colourless prismatic crystals, and the trihydrate, large, colourless, lustrous rhombs. He adds that the trihydrate is to be regarded as the more stable form. According to H. E. Schöne, the hydrated potassium salt forms transparent, colourless, lustrous, rhombohedral crystals. The white crystals of the alkali hydrosulphides may turn yellow on exposure to air. Lithium hydrosulphide becomes dark brown when heated; and molten potassium hydrosulphide appears to be black, the molten hydrate solidified to a flesh-coloured crystalline mass. W. P. Bloxam gives 455° for the **melting point** of anhydrous potassium hydrosulphide. At 450°, the edges of the crystals were fused, at 510° the mass formed a tranquil liquid. No gas was evolved at 560°, and no signs of the reaction $2KSH=K_2S+H_2S$ appear; hence, adds W. P. Bloxam, potassium hydrosulphide is therefore stable on exposure to heat, and in this respect will bear comparison with the oxygen analogue KOH. According to P. Sabatier, silica vessels are attacked by the fused alkali hydrosulphide. Trihydrated sodium hydrosulphide was found by W. P. Bloxam to have the m.p. 22°; and when heated to 360°, it loses 20·53 per cent. of sulphur. W. P. Bloxam found the crystals of hemihydrated potassium hydrosulphide to be stable in vacuo, or when heated up to 170°, but between 170° and 200°, they lose their water of crystallization and a little hydrogen sulphide, while the residue is mainly potassium hydrosulphide. H. E. Schöne and P. Sabatier dehydrated the potassium salt by heating it to 200° in a stream of hydrogen sulphide.

J. Thomsen gives for the **heat of formation** with solid sulphur (Li,S,H)aq, 66·08 Cals.; (Na,S,H)aq, 66·49 Cals.; and (K,S,H)aq, 65·1 Cals. P. Sabatier gives $Na_2S+H_2S_{gas}=NaSH+9·3$ Cals.; for the corresponding reaction with K_2S, 19 to 20·8 Cals.; and $2NaOH+2H_2S_{gas}=2H_2O_{gas}+2NaSH+16·3$ Cals. Similarly, for $2K+H_2S_{gas}+S_{solid}=2KSH+128$ Cals.; and $KOHaq+H_2Saq=HSHaq+7·7$ Cals. P. Sabatier's value for the **heat of hydration** is $NaSH+2H_2O_{liquid}=NaSH.2H_2O+5·93$ Cals., and with solid water, 3·07 Cals. The **heat of solution** found by P. Sabatier is 4·4 Cals. for NaSH, between 10° and 16°; −1·53 Cals. for $NaSH.2H_2O$ at 17·5°; R. de Forcrand gives −1·50 Cals. P. Sabatier gives for the heat of soln. of KSH, 0·77 Cals.; and for $KSH+0·5H_2O_{liquid}=0·62$ Cal. The latter number does not agree with the former when it is remembered that the water is lost only towards 200°. Probably the former is too low. The **heat of dilution** of a soln. $NaSH+4·47H_2O$ is −0·72 Cal., of a soln. $NaSH+5·68H_2O$, −1·00 Cal., and the value decreases steadily for more dil. soln., becoming zero with $NaSH+200H_2O$. P. Sabatier gives for the heat of the reaction $NaSHaq+HClaq=NaClaq+H_2Saq+6·00$ Cals.

The solid alkali hydrosulphides are hygroscopic, and readily soluble in **water.** The soln. of potassium hydrosulphide has a smell of hydrogen sulphide, has a strong alkaline reaction, and tastes alkaline and bitter. O. Bock's values for the **specific gravities** of soln. of potassium hydrosulphide of different conc., at 18° (water at 4° unity), are indicated below. F. M. Raoult gives 0·648° for the **lowering of the freezing point** per gram of anhydrous sodium hydrosulphide in 100 grms. of water, and the mol. lowering is therefore 36·3. J. W. Walker calculates that the degree of **hydrolysis** of $\frac{1}{10}N$-soln., at 25°, is 0·14 per cent. J. J. Berzelius believed that the aq. soln. of potassium hydrosulphide is not decomposed on boiling, and, in the

preparation of the salt, the latter recommends boiling the soln. to free it from an excess of hydrogen sulphide, and evaporating it to dryness. On the contrary, L. J. Thénard says that the aq. soln. is decomposed on boiling. E. Drechsel says that hydrogen sulphide is given off from the aq. soln. at 70°; D. Gernez says that the soln. loses hydrogen sulphide when a stream of air, hydrogen, or nitrogen is passed; and H. E. Schöne that by boiling the soln. 1½ hrs., potassium hydrosulphide is for the most part decomposed into the monosulphide, since boiling soln. lose hydrogen sulphide continuously and slowly. H. E. Schöne says that if boiled long enough the hydrosulphide or sulphide would be ultimately converted into the hydroxide. W. P. Bloxam found that when a 20 per cent. soln. of the hydrated salt, $KSH.\frac{1}{2}H_2O$, was boiled vigorously for 1½ hrs. in a stream of hydrogen, only 1·05 per cent. of the salt was lost by the escape of hydrogen sulphide. Hence, H. E. Schöne's statement is probably wrong, and neither of the equations $2KSH=K_2S+H_2S$, or $2KSH+2H_2O=2KOH+2H_2S$, represents the decomposition of the salt in boiling aq. soln. Similarly, W. P. Bloxam found that while an aq. soln. of sodium hydrosulphide is less stable than one of potassium hydrosulphide, "it is not true to say that a soln. of sodium hydrosulphide, on boiling, becomes converted into one of the monosulphides, Na_2S."

According to P. Bunge, the electrolysis of potassium hydrosulphide furnishes sulphur and hydrogen sulphide at the positive pole and hydrogen at the negative pole. According to O. Bock, the specific **electrical conductivities** of soln. of potassium hydrosulphide and the temp. coeff. of the conductivity at 18°, are:

Per cent.	4·09	7·86	15·08	133·43	39·22	51·22
Sp. gr.	1·0232	1·0456	1·0889	1·2124	1·2428	1·3226
Specific conductivity	0·0535	0·1039	0·1928	0·3749	0·3982	0·4003
Temp. coeff.	0·0219	0·0207	0·0191	0·0178	0·0178	0·0189

The effect of an excess of hydrogen sulphide has very little influence on the solubility of potassium hydrosulphide because, as V. Rothmund has indicated, this salt is too little ionized for the slightly dissociated hydrosulphuric acid to have an appreciable influence on the solubility.

The soln. of potassium hydrosulphide is oxidized in the **air** and becomes yellow while potassium sulphide and potassium hydroxide are formed, and later potassium thiosulphate. E. Filhol also found that very dil. soln. of sodium hydrosulphide furnish polysulphides with the deposition of sulphur and the formation of sulphate. The action of the **carbon dioxide** in the air displaces a little hydrogen sulphide; if potassium hydrosulphide be exposed to air, free from carbon dioxide, no hydrogen sulphide is evolved. Carbon dioxide acts rapidly on the salt or on its aq. soln. with the evolution of hydrogen sulphide and the formation of the corresponding carbonate. As a result, a very slight absorption of hydrogen sulphide is observed; the salt, however, remains quite white. When **sulphur** is dissolved in the soln. of alkali hydrosulphide; hydrogen sulphide is evolved, especially when heated. W. P. Bloxam studied the action of sulphur on aq. soln. of potassium hydrosulphide, and he did not succeed in isolating any compound of undoubted chemical individuality. He showed that sulphur dissolved by the soln. reacts with only a portion of the hydrosulphide yielding a polysulphide richer in sulphur than corresponds with the dissolved sulphur. The circumstance is probably due to the tendency of the soln. to form one predominating polysulphide. **Acids** displace hydrogen sulphide, and if air has access to the soln. sulphur is precipitated. The hydrosulphides are soluble in **alcohol.** A. Rule and J. S. Thomas found that alcoholic soln. of sodium or potassium hydrosulphide can dissolve sulphur to an extent represented by the formula $Na_2S_{8\cdot9}$ or $K_2S_{8\cdot9}$, but the soln. furnish only the anhydrous potassium pentasulphide, K_2S_5, or anhydrous sodium tetrasulphide, Na_2S_4.

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§ 24. Ammonium Sulphides.

According to H. Kopp,[1] the preparation of the volatile compounds of sulphur has been known from very early times ; "Basil Valentine," for example, said a blood-red oil is formed when a mixture of common sulphur, quicklime, and salammoniac is distilled ; and in the seventeenth century J. Beguin used a similar method of preparation, and the product was known for a time as *spiritus fumans sulphuratus*, or *spiritus sulphuris volatilis Bequini*. R. Boyle also drew attention to the power this liquid possessed of blackening the metals, and he termed it the *volatile tincture of sulphur*, and for some years afterwards the liquid was called *liquor fumans Boylei*. F. Hoffmann recommended the use of the liquid medicinally, and it was then called *tinctura sulphuris volatilis Fr. Hoffmanni*. F. Hoffmann also knew that cinnabar is formed by the action of the liquid on mercury. The liquid is a mixture of ammonium hydrosulphide and of several ammonium polysulphides. H. Boerhaave noted that aqua ammonia can dissolve flowers of sulphur, and on account of the similarity in the action of this liquid and liver of sulphur on metal salt soln., it was called *volatile liver of sulphur*. G. Calcagni found 100 c.c. of aqua ammonia can dissolve 1·367 grms. of sulphur. R. Kirwan (1786) also described the preparation of this product by leading what he called *hepatic air*, that is, hydrogen sulphide, into aqua ammonia. Volatile liver of sulphur is made by distillation from a mixture of sulphur with twice its weight of ammonium chloride (phosphate or sulphate), and also of lime. J. L. Gay Lussac says that free ammonia is first given off, then follows ammonium hydrosulphide in crystals which afterwards dissolve in the dark yellow distillate. C. L. Berthollet (1796) and L. N. Vauquelin (1817) also studied the product. The distillate fumes in air, but not in hydrogen, oxygen, or nitrogen ; it can dissolve more sulphur, forming an oily liquid which does not fume, and which deposits some sulphur when mixed with water.

The preparation of ammonium hydrosulphide.—In his memoir, *Sur quelques combinaisons ammoniacales et sur le rôle que joue l'ammoniaque dans les réactions chimiques* (1838), A. Bineau [2] showed that hydrogen sulphide and ammonia gas unite at ordinary or more elevated temp. volume for volume to form colourless needles or scales of ammonium hydrosulphide, $NH_3+H_2S=NH_4SH$. The combination occurs in equal volumes, says A. Bineau, in whatever proportions the two gases are mixed. A. Bineau prepared the compound by passing the two gases in equal volumes into a vessel surrounded with ice and previously filled with hydrogen or ammonia gas. W. P. Bloxam's directions are :

A wide-mouth bottle is fitted with a cork and two glass tubes to serve as inlets for the hydrogen sulphide and ammonia respectively, whilst a third tube serves as an outlet

for the escape of gases. On passing the gases, ammonia being in excess, into the bottle cooled with ice, colourless needles and scales are formed; but the greater portion is deposited on the sides of the bottle as a white, porcelain-like mass.

According to W. P. Bloxam, ammonium hydrosulphide can be prepared by this method in a state of purity, provided the volumes of gases are equal, or if the hydrogen sulphide is in slight excess, but not if the ammonia is in excess. An aq. soln. of the salt can be made by treating aq. ammonia with an excess of hydrogen sulphide. W. P. Bloxam showed that the combination does not then necessarily take place in equal proportions; the more conc. the ammonia soln., the smaller the relative proportion of hydrogen sulphide taken up by the ammonia, and compounds of the type $(NH_4)_2S.nNH_4SH$ are formed. Thus, he found that by leading a current of hydrogen sulphide into aqua ammonia of sp. gr. 0·88, when the volume ratio of aqua ammonia : water was :

$NH_4SH : (NH_4)_2S$.	1 : ⅓	1 : ½	1 : 1	1 : 2	1 : 3	1 : 4	1 : 5
Union, $NH_3 : H_2S$.	1 : 0·33	1 : 0·90	1 : 0·90	1 : 0·95	1 : 0·95	1 : 1	1 : 1

Consequently, the ammonia (sp. gr. 0·88) must be diluted with at least four times its volume of water in order that the hydrogen sulphide and ammonia may unite in equal volumes. The quantity of hydrogen sulphide taken up by one mol. of ammonia does not vary continuously with the conc., but remains constant, $NH_3 : H_2S = 1 : 1$ for wide limits when the dilution exceeds 1 : 4. It follows from the fifth of the above experiments that the most conc. soln. contains less than 19 per cent. of ammonium hydrosulphide, NH_4HS, and that corresponding with the 1 : 4 dilution contains 16 per cent. NH_4HS; consequently, the most conc. aq. soln. of ammonium hydrosulphide which can be prepared by this process contains between 16 and 19 per cent. of that salt.

W. P. Bloxam does not recommend the preparation of this salt by passing hydrogen sulphide into an alcoholic soln. of ammonia because a complex salt, $(NH_4)_2S.nNH_4S$, is obtained, and the crystals contain alcohol. R. Laming made an aq. soln. of ammonium hydrosulphide by heating ammonium carbonate or gas liquor with sodium sulphide; P. Spence, by heating the tank waste from the Leblanc soda process or gas lime with ammonium salts in a stream of steam; and J. J. Berzelius recommended subliming a mixture of ammonium chloride and potassium sulphide—not in excess.

The properties of ammonium hydrosulphide.—According to A. Bineau,[3] the sublimate forms colourless needles or plates, and W. P. Bloxam obtained it as a white porcellanous mass. The salt volatilizes and sublimes at ordinary temp., and it reacts alkaline and smells both of ammonia and of hydrogen sulphide. The **vapour density** of the mixed gases at 56·7° is 0·884; H. St. C. Deville and L. Troost found 0·89 when the calculated value for a mixture is 0·88 above 50°, therefore the vapour of ammonium hydrosulphide is only a mixture of ammonia and hydrogen sulphide, otherwise expressed, the compound in vaporizing is dissociated, $NH_4HS \rightleftharpoons H_2S + NH_3$. R. Engel and M. Moitessier removed almost all the ammonia from the mixture by means of charcoal; and at low temp. water removes almost all the same gas leaving hydrogen sulphide as a residue. As F. Isambert showed, these experiments do not give any indication of the extent of the dissociation, since, in the balanced reaction, as ammonia gas is removed from the system more of the compound would be dissociated to restore the balance. A. Horstmann found that at 57° there is no change in the density of mixtures of different proportions of the two component gases. The same result was obtained by G. Salet. F. Isambert's **compressibility** measurements show that the dissociation of the gas is practically complete. The product pv was measured at different press. for mixtures of the component gases at 33° and 40°. The quotient pv/p_1v_1 at a constant temp. for 1 to 2 atm. has a value between 1·007 and 1·008. Consequently, it is not likely that the gases undergo any marked combination, for if they did, the quotient would have a larger value.

A mixture of ammonia and hydrogen sulphide does not unite if the press. is less than a certain critical value, which depends on the temp. If the press. is at or above this value crystals of ammonium hydrosulphide are formed; if the press. be increased, more crystals will form; and if the press. be reduced, crystals will decompose. When the two gases are present in eq. amounts this press. is called the **dissociation pressure** of the solid. In the present case, if the vapour phase has the same composition as the solid with which it is in equilibrium, the system is univariant, and there is a definite dissociation press. for each temp. F. Isambert found the dissociation press. of ammonium hydrosulphide, in mm. of mercury, increases rapidly with a rise of temp.:

	4·2°	10·1°	15°	28°	32·1°	32·5°	35·6°	39·3°	44°
Vap. press. . .	132	184	259	588	748	772	919	1156	1560

J. Walker and J. S. Lumsden's results are in agreement with F. Isambert's. If ammonia or hydrogen sulphide be in excess, a two-component system is formed, and there should be a series of press. for each temp., or a series of temp. for each press., at which the system is in equilibrium. If the conc. of one of the components at a given temp. be varied, the conc. of the other component as well as the total press. of the system will vary, and the relation between these different quantities will be given by the mass law. If C_1 and C_2 be the respective conc. of the ammonia and hydrogen sulphide, then in the reaction: $NH_3+H_2S \rightleftharpoons NH_4HS$, where the ammonium hydrosulphide is a solid, with a negligbly small vap. press., C_1C_2=a constant; and if p_1 and p_2 be the respective partial press. of the two gases, and the partial press. of a gas is proportional to its conc. (Boyle's law), p_1v_1=a constant. It follows that if p_1 be greater than p_2 or p_2 greater than p_1, the product will be less than when $p_1=p_2$. *This means that an excess of either gas will hinder the dissociation of the solid.* A. Horstmann, J. Walker and J. S. Lumsden, and J. P. Magnusson have studied the dissociation press. of ammonium hydrosulphide; and J. Walker and J. S. Lumsden, the vap. press. of the alkylammonium hydrosulphides. For ammonium hydrosulphide, J. P. Magnusson finds (1) the mass law describes the relation between the partial press. of the ammonium and hydrogen sulphide over a range of 95 cm. partial press. and at one temp., namely 20°, when corrections are made for adsorption. (2) The deviations from the mass law, observed when ammonia is present in excess, are due to adsorption of the gas on the surfaces with which it is in contact, chiefly on the solid ammonium hydrosulphide. (3) The deviations from Boyle's law in the case of ammonia have been *shown to depend on a time factor, thus showing an interesting bearing of the above* experiments on our conception of the so-called imperfect gases.

The **melting point** of ammonium hydrosulphide in a closed vessel was found by E. Briner to be 120°; and, in the presence of an excess of hydrogen sulphide, the m.p. is a triple point: $NH_4SH \rightleftharpoons H_2S+NH_3$, and the equilibrium constant is K=0·04 at 22°. The **heat of vaporization** of the solid hydrosulphide, in consequence of dissociation, will be equal to the heat of formation of the solid from the component gases, viz., 22·4 Cals., as found by J. Thomsen. According to F. Isambert, the heat of vaporization between 77° and 132° is 23 Cals., and, according to J. H. van't Hoff, calculated between 9·5° and 25·1° at constant press., 22·7 Cals. J. Walker and J. S. Lumsden find that the value of this constant increases with a rise of temp., *being* 19·7 Cals. between 4·2° and 18°, and 22·0° between 30·9° and 44·4°.

J. Thomsen gives 39·03 Cals. for the **heat of formation** of the crystalline salt (N,H_5,S_{solid}), and with gaseous sulphur, 53·85 Cals. M. Berthelot gives 42·4 Cals. for the latter, and for (NH_3,H_2S), 23·0 Cals., while J. Thomsen gives 22·63 Cals. The latter also gives for aq. soln. of the salt, (N,H_4,S,H,aq), 50·6 Cals., for (NH_3,S,H_2,aq), 23·89 Cals.; and for $(2H_2Saq,2NH_3aq)$, 6·19 Cals. M. Berthelot gives −3·25 Cals. for the **heat of solution** of one part of ammonium hydrosulphide in 50 to 100 parts of water. F. M. Raoult found **the lowering of the freezing point**

of a gram of the salt in 100 grms. of water to be 0·703°, and the mol. lowering of the f.p., 35·9.

W. P. Bloxam found ammonium hydrosulphide to dissolve in water more slowly than the monosulphide, forming a colourless soln. The laboratory reagent, known as ammonium hydrosulphide or ammonium sulphide, changes on contact with air. The soln. prepared by saturating aqua ammonia with hydrogen sulphide is at first colourless, but on exposure to air, it soon acquires a yellow colour owing to the formation of polysulphides. On prolonged exposure to air, the yellow soln. loses its colour, and deposits sulphur; and when an acid is added, hydrogen sulphide is evolved, and sulphur deposited. Similarly, also the colourless soln. of ammonium hydrosulphide acquires a yellow colour on exposure to air in consequence of the formation of the thiosulphate, and, as pointed out by L. J. Thénard, of polysulphides; with a still longer exposure to air, the soln. becomes colourless, and sulphur is deposited.

According to W. P. Bloxam, a number of hypotheses have been suggested to explain the changes which occur in the oxidation of the soln.: (1) One hypothesis assumes that ammonia, water, and sulphur are first formed, and that part of the latter unites with some of the unchanged hydrosulphide, forming the disulphide, $(NH_4)_2S_2$; part forms the thiosulphate, and the remainder is precipitated. (2) Another hypothesis assumes that the hydrosulphide is directly oxidized forming mol. proportions of thiosulphate and disulphide; the latter colours the soln. yellow, and during the decolorization of the soln. sulphite and sulphate are formed. (3) According to W. P. Bloxam's hypothesis, (i) only polysulphides are formed in the first stage of the oxidation, for the aq. soln. decomposes into ammonia, water, and hydrogen sulphide, the latter is oxidized to water and sulphur; the sulphur unites with the undecomposed ammonium hydrosulphide, giving off hydrogen sulphide, and forming a polysulphide. There are no grounds for assuming that $(NH_4)_2S_2$ is the only polysulphide which is formed. The action continues until the highest polysulphide mixture possible for the given conc. is formed. The yellow colour of the soln. is then at its maximum intensity, and no oxidized sulphur is present. (ii) In the second stage of the oxidation, the polysulphides are decomposed by the oxygen of the air: $(NH_4)_2S_n+O=2NH_3+H_2O+S_n$. (iii) In the third stage, the liberated sulphur reacts with ammonia, forming ammonium sulphite and hydrosulphide: $4NH_3+3H_2O+3S=(NH_4)_2SO_3+2NH_4SH$. (iv) In the fourth stage, the sulphur reacts with the sulphite to form a thiosulphate, or with ammonium hydrosulphide to form a polysulphide. The end-product of the oxidation is ammonium thiosulphate, no sulphate appears to be formed. W. P. Bloxam also studied the analytical methods available for detecting the different ammonium-sulphur compounds in the presence of one another.

C. M. Wetherill found that ammonium hydrosulphide is soluble in alcohol, and the alcoholic soln. gradually decomposes in a badly stoppered bottle, forming ethyl sulphide, ammonia, and crystals of sulphur. W. P. Bloxam emphasizes that great care should be taken to avoid the inhalation of the vapours of the ammonium-sulphur compounds, since marked physiological effects are produced, even when but small quantities are present in the air respired. Vapours of the ammonium sulphides produce much more serious effects than hydrogen sulphide, the toxic effect being greater in proportion to the volatility of the sulphide; the most dangerous compound is the volatile, oily liquid, ammonium diammino-monosulphide, $(NH_4)_2S.2NH_3$.

The preparation of ammonium monosulphide, $(NH_4)_2S$.—A. Bineau [4] prepared this salt by passing dry hydrogen sulphide, mixed with twice its volume of dry ammonia gas, through a tube cooled to $-18°$: $2NH_3+H_2S=(NH_4)_2S$; while, if a greater proportion of ammonia be present, the excess remains uncombined; and he adds that at ordinary temp., only the hydrosulphide is formed: $NH_3+H_2S=NH_4SH$. W. P. Bloxam has shown that these statements are not correct. If a mixture of the dried gases with a considerable excess of ammonia be conducted

into a flask cooled to $-18°$, not only mica-like crystals of ammonium monosulphide appear, but a white mass of ammonium hydrosulphide and fern-like crystals of what W. P. Bloxam considers to be $(NH_4)_2S.nNH_4HS$, are also produced. When removed from the freezing mixture, the crystals of ammonium monosulphide decompose with the evolution of ammonia; if iced-water be added to the contents of the flask, the monosulphide rapidly dissolves, while the white porcelain mass of hydrosulphide passes into soln. rather slowly. Hence, if the liquid be decanted immediately, analyses of the soln. show that the ratio $NH_3 : H_2S$ is as $2 : 1$. If a still greater excess of ammonia be employed an oily liquid of the composition $(NH_4)_2S.2NH_3$—ammonium diammino-sulphide—is formed. However, by carefully adjusting the volumes of the gases and the rate of flow, it is possible to prepare ammonium monosulphide in micaceous crystals.

The usual method of making a soln. of ammonium monosulphide is to divide a quantity of aqua ammonia into equal parts; one part is sat. with hydrogensulphide, and then mixed with the untreated part. W. P. Bloxam has pointed out that conc. soln. of this salt cannot be prepared in this way because the conc. is limited by the need for diluting the soln., so that the hydrosulphide may be formed, without the complex $(NH_4)_2S.nNH_4SH$. If the latter were to be produced, the mixed soln. would contain an excess of ammonia, and the complex might not be resolved into ammonium sulphide when mixed with the aqua ammonia. W. P. Bloxam further showed that the other method for making the soln., namely, by passing hydrogen sulphide in quantity just sufficient to form ammonium monosulphide, entails analysis of the soln. at intervals, in order to guard against the introduction of excess of hydrogen sulphide. He says that it is possible to determine qualitatively or quantitatively any excess either of ammonia or of hydrogen sulphide over and above that required to form ammonium monosulphide by the method of E. Divers and T. Shimidzu with manganous sulphate, or preferably with copper sulphate, the copper salt giving the sharper reaction. The following reaction is stated to occur with ammonium hydrosulphide: $2CuSO_4+2NH_4SH=2CuS+(NH_4)_2SO_4+H_2SO_4$; and with ammonium monosulphide: $CuSO_4+(NH_4)_2S=CuS+(NH_4)_2SO_4$, and also $2CuSO_4+(NH_4)_2S+2NH_4OH=CuS+Cu(OH)_2+2(NH_4)_2SO_4$. The examination conducted is as follows:

An excess of a soln. of recrystallized cupric sulphate (1 c.c. = about 0·1 grm. $CuSO_4$) is placed in a flask, water is added, and the soln. to be examined is run in. The flask is closed by a tightly fitting cork, and the flask and contents shaken; the reaction is very sharp, and the air in the flask, after once shaking, is invariably free from hydrogen sulphide. The supernatant liquor is filtered, and the precipitate remaining in the flask is washed with hot water by decantation until free from acidity and copper salt. The filtrate is allowed to cool, and titrated with decinormal soln. of potassium hydroxide. If the first drops produce a turbidity, showing that the mixture has not become acid, ammonia soln. is added to the precipitate remaining in the flask, which is well shaken. On filtering, a deep blue soln. is obtained, showing that an excess of ammonia over that required to form ammonium monosulphide was present. A soln. containing ammonia and hydrogen sulphide in the exact proportions required by ammonium monosulphide develops no acidity, and the precipitate, after treatment with ammonia, does not yield a blue filtrate. To determine any excess of ammonia quantitatively, it is only necessary to add to the cupric sulphate soln. in the flask an excess of standard acid, and to proceed as above, the difference between the acid taken and that found by titration corresponding to the excess of ammonia present.

Hence, to prepare a conc. soln. of ammonium monosulphide, a current of washed hydrogen sulphide is passed into conc. aqua ammonia cooled to 0° until the neutral point is reached. Attempts to obtain crystals by cooling the soln. to $-40°$ were not successful. W. P. Bloxam believes that the soln. so obtained is not really the monosulphide at all, but rather a soln. of a mol. of the complex $(NH_4)_2S.2NH_4SH$ in two mols. of ammonium hydroxide, NH_4OH; because of (i) its action on cupric sulphate; (ii) its failure to yield crystals by cooling, attributed to the solvent action of free ammonia; and (iii) because it exhibits no tendency to dissolve sulphur.

Indeed, the soln. evolves hydrogen sulphide and forms a crystalline compound, $(NH_4)_4S_9$, when rather more sulphur has gone into soln. than is required to form $(NH_4)_2S_2$. He explains the action as follows:

When hydrogen sulphide is passed into ammonia soln. $(NH_4)_2S$ is first formed, and this breaks *down giving NH_4HS and NH_4OH. The NH_4HS thus produced unites with more* $(NH_4)_2S$ to form compounds of the general formula $(NH_4)_2S.nNH_4HS$, the value of n increasing with the dilution of the soln. With the strongest ammonia soln., the sat. product has the composition $(NH_4)_2S.2NH_4HS$.

E. Donath prepared a conc. aq. soln. by distilling ammonium chloride with a hot soln. of sodium sulphide until half the liquid has passed to the receiver. E. W. Parnell and J. Simpson patented a process for making ammonium sulphide by heating the mixed residues of the Leblanc and ammonia-soda processes; they also used calcium or barium sulphide instead of the Leblanc residue. Ammonium carbonate with calcium or barium sulphide can also be used: $(NH_4)_2CO_3+BaS =BaCO_3+(NH_4)_2S$. According to J. Habermann, ammonium sulphide free from arsenic can be obtained only by using materials free from that element.

The properties of ammonium monosulphide.—The crystals of ammonium monosulphide, $(NH_4)_2S$, have a strong alkaline reaction, and, according to A. Bineau, when exposed at ordinary temp., they readily lose half the combined ammonia. H. St. C. Deville and L. Troost found the vapour density of ammonium monosulphide to be 1·26 and 99·5°. R. Engel and A. Moitessier[5] say the compound dissociates rapidly when the temp. is raised, and at 45°, the dissociation is complete: $(NH_4)_2S=2NH_3+H_2S$; vapour density observations agree with this observation. This is shown by the work of A. Horstmann, J. C. G. de Marignac, and G. Salet who observed that if one volume of hydrogen sulphide be mixed with an equal volume of ammonia, and then with a third equi-volume of the same gas, no perceptible contraction occurs. F. Isambert found that if one component is in excess, the vap. press., especially at high temp., is smaller than the sum of the vap. press. of ammonium sulphide and of the free gases. R. de Forcrand's value for the **heat of formation,** (N_2,H_8,S_{solid})aq, is 56·8 Cals.; and for the **heat of solution,** −8·0 Cals.; consequently, the heat of formation of the anhydrous solid from its elements is 64·8 Cals. M. Berthelot gives for the **heat of neutralization,** $2NH_3aq+H_2Saq = \ldots +6{\cdot}2$ Cals.

The aq. soln. is a colourless alkaline liquid which smells both of ammonia and hydrogen sulphide. Unlike E. Priwoznik, K. Heumann found that the conc. aq. soln. reacts with copper giving off hydrogen, and forming rhombic cuprous sulphide, Cu_2S, and that a not inconsiderable amount of copper passes into soln. Cupric oxide, CuO, reacts: $2CuO+2(NH_4)_2S=Cu_2S+4NH_3+H_2O+S$, and some cupric sulphide, CuS, is simultaneously formed. Pulverulent silver is not attacked. F. C. Schneider noted that palladous chloride paper is blackened by ammonium sulphide; and G. Buchner showed that when soln. of the complex alkali zinc, cobalt, nickel, ferrous or ferric pyrophosphates are treated with a soln. of ammonium monosulphide, zinc, cobalt, nickel, ferrous, or ferric sulphides are respectively precipitated, and the manganese, uranium, chromium, or aluminium salts give no precipitate.

L. Troost described three different products of the action of hydrogen sulphide with an excess of ammonia, but they were not investigated much further. E. C. Franklin found that ammonium sulphide, $(NH_4)_2S$, is soluble in liquid ammonia. By treating a large excess of ammonia, with hydrogen sulphide in a flask cooled to −18°, W. P. Bloxam obtained a highly refracting yellow oil which was more volatile than ammonium monosulphide, and which, when removed from the freezing mixture, bubbled up and gave off ammonia leaving a residue of ammonium hydrosulphide. The composition of the oil corresponded with **ammonium diammino-monosulphide,** $(NH_4)_2S.2NH_3$. These crystals can be regarded as $H_2S(NH_3)_4$. E. Maumené obtained fine crystals from a very conc. soln. of ammonium hydrosulphide in aqua

ammonia at 0° ; they had a composition corresponding with **ammonium tetrammino-sulphide,** $(NH_4)_2S.4NH_3$, otherwise expressed, with $H_2S(NH_3)_6$.

W. P. Bloxam prepared a number of products which he regarded as complexes of the composition $(NH_4)_2S.nNH_4SH$, by conducting a mixture of ammonia and hydrogen sulphide into a flask cooled with ice ; by saturating conc. aqua ammonia with hydrogen sulphide ; and by passing hydrogen sulphide into a soln. of dry ammonia in absolute alcohol. By working under different conditions of temp., etc., crystalline products with $n=2$, 12, 18, and 24 were obtained. There is nothing here to show whether these substances are chemical individuals or mixed crystals.

The methods which have been reported for preparation of **ammonium disulphide,** $(NH_4)_2S_2$, by the dissolution of the theoretical amount of sulphur in ammonium monosulphide, were specially studied by W. P. Bloxam [6] in his memoir: *The sulphides and polysulphides of ammonium.* He sealed up the calculated quantity of sulphur in a tube with a soln. of ammonium monosulphide. He noticed an evolution of gas occurred as the sulphur dissolved, a phenomenon which he thinks would not be observed if $(NH_4)_2S$ were really the solute. W. P. Bloxam also failed to obtain the disulphide by passing through a hot tube the vapour of ammonium chloride and sulphur, and he finally concluded that up to the present ammonium disulphide has not been prepared either in the solid state or in soln. J. Fritzsche also failed to make the disulphide nearly 60 years earlier than W. P. Bloxam. R. de Forcrand calculated that the heat of formation of the unknown solid will prove to be $(N_2,H_8,S_2)_{solid}=(NH_4)_2S_{2solid}+66{\cdot}2$ Cals.

Ammonium trisulphide, $(NH_4)_2S_3$, a soln. of this salt was obtained by W. P. Bloxam [7] by adding cold air-free water to crystals of ammonium pentasulphide, $(NH_4)_2S_5$, in a wide-necked flask until the addition of a little water produced no further precipitation of sulphur. The golden-yellow liquid so obtained contains ammonia and sulphur in the ratio required for ammonium trisulphide. J. Fritzsche found a small deficiency of sulphur when using a similar process. W. P. Bloxam attempted to make this compound by gradually warming to 70°–80° a mixture of the theoretical quantities of a soln. of ammonium monosulphide and sulphur in a sealed tube. All the sulphur dissolved, and the orange-red liquid deposited rosetted needles of ammonium pentasulphide, $(NH_4)_2S_5.H_2O$. Attempts by J. Fritzsche and W. P. Bloxam to make the solid salt have failed. K. A. Hofmann and F. Höchtlen agitated a 10 per cent. soln. of auric chloride with a soln. prepared by saturating a 25 per cent. soln. of ammonium hydrosulphide with sulphur, at 30°, and obtained crystals with the composition NH_4AuS_3, **ammonium aurotrisulphide,** in which they believe the gold is univalent.

According to E. Priwoznik, when **copper** is allowed to stand in contact with a soln. of an ammonium polysulphide, cupric sulphide is formed, and after a long time cuprous sulphide, and, a colourless soln. of ammonium monosulphide appears ; on the other hand, V. Merz and W. Weith found some hydrogen is developed, and rhombic crystals of a complex of cuprous sulphide and ammonium sulphide is produced. K. Heumann confirmed the fact that hydrogen is developed, and he assigned the formula, $(NH_4)_2Cu_2S_7$, to the red complex ; E. Priwoznik, V. Merz and W. Weith, and H. Peltzer found that in contact with a soln. of ammonium polysulphide, metallic **silver** becomes covered with a thick crust of silver sulphide, Ag_2S ; with **tin,** a soluble sulphide is formed ; **nickel** behaves like tin and the soln. becomes black ; **iron** gradually becomes coated with a black film of ferrous sulphide ; **copper oxide** imparts a red colour to the soln. in consequence of the formation of the complex $(NH_4)_2Cu_2S_7$; **lead mono-oxide** and **lead di-oxide** form crystals of lead sulphide ; **ferrous oxide** is not perceptibly changed ; and **cadmium oxide** forms the corresponding sulphide, slowly in the cold, and rapidly when heated ; and **manganese oxide** similarly forms flesh-coloured manganese sulphide, MnS.

As previously indicated, when W. P. Bloxam attempted to make ammonium disulphide, he obtained crystals which, when rapidly dried between filter paper gave analytical numbers corresponding with *tetrahydrated tetrammonium heptasulphide,* $(NH_4)_4S_7.4H_2O$, but there

is no other evidence that this product is a chemical individual. It dissolves in water forming a yellow soln. which can be kept a long time before it deposits sulphur.

Ammonium tetrasulphide, $(NH_4)_2S_4$.—J. Fritzsche obtained long sulphur-yellow crystals of what he regarded as ammonium tetrasulphide by passing hydrogen sulphide and ammonia alternately through a soln. of ammonium pentasulphide. P. Sabatier obtained a similar result. W. P. Bloxam attempted to make this same salt by heating in a sealed tube to about 80°, a soln. of ammonium monosulphide with the calculated quantity of sulphur, but the deep red soln. furnished a mass of yellow needles of *hemiheptahydrated tetrammonium enneasulphide*, $(NH_4)_4S_9.3\frac{1}{2}H_2O$. He then proceeded as described by J. Fritzsche, until a mass of crystals had formed: he then poured off the mother liquid, and dissolved the crystals in a small quantity of water at 40°–50°. The cooling liquid furnished crystals of the hydrated pentasulphide. The mother liquid was poured off, and the crystals warmed at 20°–30°; they melted in their water of crystallization, and on cooling furnished fine yellow crystals of hydrated ammonium tetrasulphide, $(NH_4)_2S_4.\frac{1}{4}H_2O$. Hence, the crystalline mass obtained by J. Fritzsche's method can be separated into ammonium tetra- and penta-sulphide. J. Fritzsche states that his salt is easily soluble in water without decomposition, and a conc. soln. can be kept without decomposition if well-boiled water has been used as solvent. On the contrary, W. P. Bloxam says that ammonium tetrasulphide is at once decomposed by water with the deposition of sulphur, and he explains J. Fritzsche's result by assuming that his product is not the pure sulphide, but rather contains the tetrasulphide admixed with the complex groups $(NH_4)_2S.nNH_4HS$. The presence of these groups prevents the precipitation of sulphur from a conc. soln., and retards its precipitation if such a soln. be diluted.

A dil. soln. of J. Fritzsche's salt gradually deposits sulphur; and, according to P. Sabatier, when the aq. soln. is treated with hydrochloric acid, it deposits three-fourths of the contained sulphur, and evolves hydrogen chloride. J. Fritzsche says his salt is soluble in alcohol. K. A. Hofmann and F. Höchtlen obtained complexes with cuprous and bismuth salts. P. Sabatier, and R. de Forcrand found the heat of formation of the solid (N_2H_8,S_{4solid}), 69·06 Cals., and of the aq. soln., 60·80 Cals. P. Sabatier also found that the heat of soln. of a gram-eq. of $(NH_4)_2S_4$ in 150 parts of water at 11·5° is −8·2 Cals.; the heat of the solid $(2NH_{3gas},H_2S_{gas},S_{3solid})$, 40·0 Cals.; and the heat of the reaction with a mixture of iodine and hydrochloric acid at 12°, 3·30 Cals. per gram-eq.

Tetrammonium enneasulphide, $(NH_4)_4S_9$.—According to W. P. Bloxam, crystals of hemiheptahydrated tetrammonium enneasulphide, $(NH_4)_4S_9.3\frac{1}{2}H_2O$, are formed in an attempt to make ammonium tetrasulphide, as indicated above. He found that this same tetrammonium enneasulphide is formed on warming a moderately strong soln. of $(NH_4)_2S$ with excess of sulphur in an open vessel, until no more of the latter is dissolved, allowing to cool, pouring off the deep red soln. from the excess of sulphur, and cooling in a freezing mixture, a yellow crystalline mass is deposited; this, on gently warming, dissolves in its own water of crystallization, forming a deep red liquid. W. P. Bloxam also added that the sat. red liquor obtained by the action of a soln. of $(NH_4)_2S,2NH_4.HS$ on sulphur cannot be induced to take up more sulphur than enough to form tetrammonium enneasulphide $(NH_4)_2S_9$, nor can a soln. of ammonium monosulphide be made to take up more sulphur than is required for the formation of this same compound. It would therefore appear that all the simple or diammonium polysulphides obtained are secondary products, formed by the decomposition of tetrammonium enneasulphide under varying conditions of temp., conc., etc. Thus, when the original sat. red soln. of the enneasulphide are of suitable strengths, the following simple or diammonium penta-, hepta-, and ennea-sulphides can be obtained; but in all cases the mother liquors left after separation of the crystals have a lower sulphur value than is required by $(NH_4)_4S_9$.

Ammonium pentasulphide, $(NH_4)_2S_5$.—J. Fritzsche prepared this salt by

saturating aqua ammonia with hydrogen sulphide, and adding finely powdered sulphur while ammonia gas is being passed into the liquid. The excess of ammonia is then sat. by a current of hydrogen sulphide, the soln. again treated with sulphur, ammonia, and the hydrogen sulphide yet again. After the final saturation, the soln., if kept cold, solidifies to a mass of crystals. The crystalline mass is melted by heating it to 40° or 50°, and allowed to cool slowly while excluded from contact with air. Long orange-yellow rhombic crystals are formed. W. P. Bloxam prepared similar crystals by diluting 200 c.c. of a 40 per cent. soln. of ammonium monosulphide with 75 c.c. of water, and adding finely powdered sulphur in excess of that required for the formation of the pentasulphide. The mixture was gradually warmed up to 80°. Hydrogen sulphide was evolved, and sulphur dissolved so as to form a deep red liquid. When the action had ceased, the clear decanted liquid deposited a fine crop of crystals of the desired compound on standing over-night. When a more conc. soln. was employed, and the mixture heated in a sealed tube to 100°, the crystals were mixed with free sulphur. W. P. Bloxam also made ammonium pentasulphide by diluting aqua ammonia, sp. gr. 0·880, with its own volume of water, mixing it with an excess of finely powdered sulphur, and treating it with hydrogen sulphide until the temp. of the soln. falls, and no more of the gas is absorbed. The sulphur dissolves rapidly, and the deep red filtered liquid, on standing 24 hrs., deposits a small crop of crystals of the pentasulphide—the mother liquid retains $(NH_4)_4S_9$. Indeed, in all cases, W. P. Bloxam supposes that the soln. contains tetrammonium pentasulphide. W. P. Bloxam also heated a soln. of ammonium monosulphide with the amount of finely divided sulphur required for the formation of the pentasulphide in a sealed tube at 80°, when a mass of small needle-shaped crystals was suddenly formed; when the mixture was heated to 100° a little sulphur dissolved, but even at 120°, very little more sulphur dissolved in three more hours. The large residue of sulphur which remained shows that the power of dissolving sulphur possessed by soln. of ammonium sulphide is greatly below the limits required for the pentasulphide. H. G. Byers added 95 per cent. alcohol to a conc. soln. of ammonium sulphide, sat. with sulphur—volume for volume—and after the mixture had stood for a few hours, obtained crystals of the pentasulphide. W. P. Bloxam prepared **monohydrated ammonium pentasulphide,** $(NH_4)_2S_5.H_2O$, *by heating tetrahydrated tetrammonium heptasulphide to* 70°–80°, when it forms an orange-red soln. which when cooled furnishes crystalline masses of fine needle-like crystals of the desired salt.

Anhydrous ammonium pentasulphide furnishes orange-yellow rhombic crystals, which J. Fritzsche says decompose when heated, forming volatile ammonium monosulphide, and residual heptasulphide: $3(NH_4)_2S_5=2(NH_4)_2S_7+(NH_4)_2S$—a similar result is obtained by keeping the crystals in a large vessel full of air, and if the crystals are moist, they become a ruby colour. *The crystals are gradually oxidized to a mixture of sulphur and ammonium thiosulphate when exposed to the open air,* ammonium monosulphide is at the same time evolved; this decomposition proceeds much more slowly in air dried by sulphuric acid. J. Fritzsche found the crystals are decomposed by water with the separation of sulphur, and, according to W. P. Bloxam, the aq. soln. then contains ammonium trisulphide. J. Fritzsche adds that the pentasulphide dissolves completely in alcohol, but the soln., even when kept in closed vessels, deposits crystals of sulphur. K. A. Hofmann and F. Höchtlen prepared complexes with platinum, iridium, and palladium. According *to P. Sabatier and R. de Forcrand, the heat of formation is* $(Na_2,H_8,S_5)_{solid}=69·46$ Cals.; and the former found $(2NH_{3gas},H_2S_{gas},S_{solid})=(NH_8)_5S_{2solid}+40·4$ Cals.; the heat of soln. of 3·12 to 10·65 grms. of the salt in 500 c.c. of water at 13° to be −8·4 Cals. per gram-eq.; and the heat developed by its decomposition with iodine and hydrochloric acid, 24·2 Cals.

Ammonium heptasulphide, $(NH_4)_2S_7$.—J. Fritzsche reported that crystals of this salt are formed by the spontaneous vaporization of crystals of the pentasulphide; melting crystals of the pentasulphide in their own mother liquid, and

exposing the soln. under the receiver of an air pump, ammonium monosulphide is evolved, $3(NH_4)_2S_5=(NH_4)_2S+2(NH_4)_2S_7$, and ruby-red crystals of the heptasulphide are formed, and finally crystals of the undecomposed pentasulphide are deposited. J. Fritzsche also said that the heptasulphide is formed while the mother liquid is being drained from the pentasulphide in the absence of air. He adds:

After some days, many of the crystals of the pentasulphide carried new, small, ruby-coloured crystals, and others bore cavities sideways which were filled up with the new substance; that, however, only adhered loosely to the crystal out of which it had been formed. The decomposition becomes complete on standing for a longer time, especially when the vessel is large and filled with dry air. The new compound appears then in the form of a crystalline crust, resembling in shape the original crystal, but larger and hollow in the centre.

Under these conditions W. P. Bloxam obtained crystals of sulphur and of the pentasulphide, but no ruby-red crystals of the heptasulphide, and he obtained the enneasulphide by working according to J. Fritzsche's directions. P. Sabatier claims to have made the heptasulphide by digesting sulphur with the warm or cold mother liquid remaining after the separation of crystals of the pentasulphide. P. Sabatier's analysis corresponds with *ammonium octosulphide*, $(NH_4)_2S_8$. W. P. Bloxam made crystals of the hydrated salt, $(NH_4)_2S_7.\frac{4}{5}H_2O$, by the simultaneous action of sulphur and hydrogen sulphide on aqua ammonia rather more conc. than that used in the preparation of the pentasulphide.

200 c.c. of aqua ammonia (of sp. gr. 0·880) were diluted with 60 c.c. of water, excess of sulphur added, and hydrogen sulphide passed to saturation, the flask and contents being kept in constant agitation to promote soln. When the hydrogen sulphide passed through the soln. without being absorbed, and the temp. of the soln. began to fall, the latter was carefully poured off from the undissolved sulphur into another flask. Small glistening, red crystals at once began to form, and continued to increase even when the flask was placed in warm water.

According to W. P. Bloxam, the dried crystals of the hydrate are polychroïc, and exhibit a peculiar violet lustre. J. Fritzsche reported that the crystals of the anhydrous salt can be preserved in bottles completely filled with them, and protected from heat and light; they change when exposed to air, but not so quickly as the pentasulphide. The crystals of the hydrated salt retain their tetrahedral form in air, but become slowly coated with sulphur. When the anhydrous salt is heated, the crystals become bright red, and at a temp. not much higher than the m.p. of sulphur they decompose, giving off a lower sulphide—or may be the hydrosulphide—which is deposited on the sides of the vessel in yellow drops, and leaving a residue of sulphur. The heptasulphide is decomposed by water more slowly than the pentasulphide, forming a pale yellow soln. with the deposition of sulphur. J. Fritzsche also adds that hydrochloric acid attacks the anhydrous salt more slowly than the pentasulphide; and, according to W. P. Bloxam, the hydrated salt is attacked faster than in the enneasulphide. According to P. Sabatier and R. de Forcrand, the heat of formation of the anhydrous solid is $(N_2,H_8,S_8)_{solid}$, 69·66 Cals.; P. Sabatier also gives for $(2NH_{3gas},H_{2gas},S_{8solid})$, 40·6 Cals.; for the heat of soln. for an eq. in an excess of water at 11° is −8·6 Cals.; and 24·0 Cals. for the heat developed during the decomposition of the salt with iodine and hydrochloric acid. In consequence of the agreement in the thermochemical data for the penta- and hepta- (P. Sabatier says octo-) sulphide, P. Sabatier thinks it possible that in both compounds all but four of the sulphur atoms per molecule are not chemically but molecularly united in the compound.

Ammonium enneasulphide, $(NH_4)_2S_9$.—This compound represents the highest ammonium sulphide which has yet been prepared. W. P. Bloxam obtained this salt by diluting 500 c.c. of aqua ammonia with 150 c.c. of water, and treating the soln. simultaneously with hydrogen sulphide and an excess of sulphur. The

deep red soln. of tetrammonium enneasulphide, $(NH_4)_4S_9$, so obtained deposits crystals of the pentasulphide, $(NH_4)_2S_5$, on standing. When the red mother liquid in a large flask, fitted with a loosely fitting cork, was allowed to stand some months, a large crop of aggregates of small, hard, shining, deep red crystals was deposited. These conditions are similar to those employed by J. Fritzsche for the preparation of the heptasulphide, but the analyses correspond closely with the requirements for hemihydrated ammonium enneasulphide, $(NH_4)_2S_9.\frac{1}{2}H_2O$; and the mother liquor from these crystals, likewise preserved in a loosely corked flask, furnished crystals of the $\frac{4}{5}$-hydrated ammonium enneasulphide, $(NH_4)_2S_9.\frac{4}{5}H_2O$. If the crystals be rapidly freed from the mother liquor, only a thin film of sulphur is formed on them; if treated with water, they are decomposed, and dissolve to a limited extent, yielding a pale yellow soln. of a lower sulphide, whilst a sulphur-coated crystal is left preserving the form of the original. The behaviour of this salt with acids is characteristic; the exterior of the crystal becomes coated with a hard mass of sulphur, which protects it against the action of dil. hydrochloric acid, even when boiled with it. The crystals of diammonium enneasulphide, if pressed with a glass rod against a hard surface, fly to pieces, the powder having the colour of finely divided potassium dichromate.

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§ 25. The Alkali Sulphates

The alchemists of the Middle Ages remarked on the formation of the potassium sulphate—normal or acid—as a residual product during the preparation of nitric acid by the action of sulphuric acid on saltpetre. In his *Opera mineralis*, for example, Isaac Holland, about the fifteenth century,[1] mentioned the formation of this salt during the preparation of nitric acid. Robert Boyle and J. R. Glauber [2] also obtained potassium sulphate—*tartarus vitriolatus*—by the action of sulphuric acid—*oil of vitriol*—on potassium carbonate—*sal tartari*, or *tartar*. In 1663, C. Glaser also described the preparation of potassium sulphate, afterwards called *sal polychrestum Glaseri*, by the action of sulphur on fixed nitre—if insufficient sulphur be used, a mixture of sulphate and nitrate is formed which when cast into little balls was called *prunella salt*. J. R. Glauber also in his *Tractatus de natura salium*, noted the formation of decahydrated sodium sulphate, $Na_2SO_4.10H_2O$, and he ascribed to *sel mirabile*, as he called it, exaggerated virtues as a medicine. The *sel mirabile Glauberi* is now often called *Glauber's salt*. Some of the early names for *potassium sulphate* were: *tartarus vitriolatus*, or vitriolized tartar; *arcanum duplicatum*; *sal polychrestum Glaseri*; *sal de duobus*; *specificum purgans Paracelsi*; *panacæa holsatica*; *panacæa duplicata*; *nitrum vitriolatum*; *spiritus vitrioli coagulabilis*. The sulphates of the other alkali salts were naturally prepared soon after the discovery of the respective bases.

The occurrence of sodium sulphate.—The mineral *thénardite* is anhydrous sodium sulphate; it is found in Tarapaca, Atacama, Balchasch Sea (Central Asia), Rio Verde (Arizona), etc. *Glauberite* is a double sulphate of sodium and calcium, $Na_2SO_4.CaSO_4$, found in the borax lakes (San Bernardino), Mayo salt mines (Pendschab), Westeregeln (Stassfurt), Priola (Sicily), etc. *Astrakanite*, or *simonite*, or *blœdite*, a hydrated double sulphate of sodium and magnesium, $Na_2Mg(SO_4)_2.4H_2O$; there are also *vanthoffite*, $MgSO_4.3Na_2SO_4$; and *löwite*, $MgSO_4.Na_2SO_4.2\frac{1}{2}H_2O$, found in the Stassfurt salt deposits.

A kind of soda alum, $Na_2SO_4.Al_2O_3.24H_2O$, *mendozite*, has been reported from San Juan (Argentine), Shimane (Japan), etc.; *tamarugite*, reported from Cerros Pintados (Chili), is like soda alum, but with only half the amount of water present in the normal salt. In *strüvenite* from Copiapo, half the soda is replaced by magnesia. *Tychite* [3] has the composition $Na_6Mg_2(CO_3)_4SO_4$, or $2MgCO_3.2Na_2CO_3.Na_2SO_4$. The crystals of *hanksite* from the borax lake of San Bernardino (Cal.) contain $9Na_2SO_4.2Na_2CO_3.KCl$ or $Na_{22}K(SO_4)_9(CO_3)_2Cl$; and *sulphohalite* [4] from the same locality, $3Na_2SO_4.2NaCl$, or $Na_6(SO_4)_2ClF$. Monoclinic crystals of *darapskite*, $Na_2SO_4.NaNO_3.H_2O$, are found in the nitre beds of Pampa del Toro (Chile). *Urasite*, found near the Caspian Sea, and *sideronatrite*, found near Haantajaya (Chili), appear to be the same mineral, approximating to $2Na_2O.Fe_2O_3.4SO_3.7H_2O$; *ferronatrite*, also from Chile, approximates $3Na_2SO_4.Fe_2(SO_4)_3.6H_2O$.

Sodium sulphate occurs in small quantities in soln. in sea-water, and in some lakes, mineral springs, etc. Calcium and magnesium sulphates or double sulphates of magnesium with calcium or sodium are first deposited during the evaporation of sea-water, then follow anhydrite, polyhalite, and kieserite; the waters of saline lakes containing a high proportion of sodium sulphate and little calcium or magnesium, may deposit sodium sulphate in considerable quantities determined by the temp. as affected by the season of the year. The Siberian lakes—Altai, Beisk, Domoshakova, Shunett, and Kiesil-Kul—deposit sodium sulphate. It has been estimated [5] that in addition to the Glauber's salt in soln., the Great Marmyshansk Lake contains 2,600,000 tons of crystallized decahydrated, and 397,210 tons of the dried sulphate; the Little Marmyshansk Lake, 451,400 of the crystallized decahydrate; Lake Tuskal, 1,805,500 tons; and Lake Varche, 1,805,500 tons. G. K. Gilbert [6] says in the Great Salt Lake, and in the Karaboghaz, *mirabilite*, or decahydrated sodium sulphate, $Na_2SO_4.10H_2O$, is deposited in winter; and L. Mrazec and W. Tierseyre say it is formed on the surface of Lake Sarat (Roumania)

in winter, and dissolved in summer. Similar remarks apply to Lake Sevier (Utah). Sodium sulphate is found as an efflorescence on the edges of some streams on the Cordillieras, and deposits of this salt are found on the Wyoming Plateau (Laramie). H. Pemberton and G. P. Tucker[7] report a sample of the "solid soda" of this district with Na_2SO_4, 36; $CaSO_4$, 1·45; $CaCl_2$, 0·77; NaCl, 0·21; H_2O, 46·87; and insoluble matter, 13·86 per cent. A. Smith has shown that sulphates are present in the air of towns where the sulphuric acid converts the sodium chloride into sodium sulphate; the former salt—sodium chloride—is found in the atm. over and near the sea owing to the evaporation of fine spray. The fact that supersaturated soln. of sodium sulphate crystallize if exposed to the air, while supersaturated soln. of other salts remain liquid under the same conditions, is taken by F. Parmentier to prove the presence of minute crystals of sodium sulphate in the atm. R. Zaloziecky[8] reported crystals of sodium sulphate in a cleft in the kainite beds of Kalusz of Galicia; C. F. Rammelsberg, and O. Popp, in the natron of Egypt; H. Haw, in boronatrocalcite; V. l'Olivier, in Peruvian nitrates; R. Kemper and K. Kraut in Peruvian guano; and H. van Erp, in the efflorescence found on walls.

The occurrence of potassium sulphate.—Potassium sulphate has been reported in volcanic lava—*e.g.* the *glaserite* or *aphthitalite*, $K_3Na(SO_4)_2$, found as an incrustation on Vesuvian lava, and in the salt deposits of Douglashall (Westeregeln), at Rucalmuta (Sicily), etc. B. Gossner[9] regards glaserite as a definite mineral species, but J. H. van't Hoff and H. Barschall consider it to be a mixture of the two component sulphates: $3K_2SO_4+Na_2SO_4$. The waters in volcanic districts also contain a little—say, 0·15 per cent.—of potassium sulphate. The double or triple sulphates of potassium and calcium or magnesium in the Stassfurt deposits are of great importance. There are: *kainite*, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$; *picromerite* or *schönite*, $K_2SO_4.MgSO_4.6H_2O$; *polyhälite*, $K_2SO_4.MgSO_4.2CaSO_4.2H_2O$; *krugite*, $K_2SO_4.MgSO_4.4CaSO_4.2H_2O$; *langbeinite*, $2MgSO_4.K_2SO_4$; *leonite*, $MgSO_4.K_2SO_4.4H_2O$. The mineral *syngenite*, $K_2SO_4.CaSO_4.H_2O$, is found in cavities in the rock-salt at Kalusz (Galicia); *cyanochroite* or *cyanochrome*, $K_2SO_4.CuSO_4.6H_2O$, and *chlorochroïte*, $K_2SO_4.CuCl_2$, are secondary products of the action of volcanic gases on volcanic lavas. There is also the so-called *kalinite*, a kind of potash alum found as an efflorescence on some volcanic lava, and in the rock-salt at Saarbrücken, etc. *Alunite*, from Italy, Hungary, Colorado, etc., approximates $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$.

The preparation of sodium sulphate.—Comparatively little sodium sulphate is used in the hydrated form as crystallized sodium sulphate, $Na_2SO_4.10H_2O$, or Glauber's salt, and that little is used mainly for pharmaceutical purposes, and in veterinary practice. The great bulk manufactured is calcined to form anhydrous sodium sulphate or *salt-cake*. A little salt-cake is used in glass-making, but much the larger proportion is manufactured directly into alkali carbonate. Crystallized sodium sulphate can be obtained by the evaporation of many spring waters, and the mother liquor from the evaporation of sea-water may also deposit crystals of Glauber's salt at low temp. At ordinary temp., a mixture of magnesium sulphate and sodium chloride is formed—*sels mixtes*—but, as C. W. Scheele[10] observed in 1779, if the temp. be reduced, hydrated sodium sulphate alone crystallizes from the soln.; and, as H. Rose observed, if the evaporation be conducted above 50°, the soln. again deposits sodium sulphate, but in the anhydrous form. These results can be readily interpreted in the light of the solubility curve, Fig. 46, and the law of mass action. In a similar manner, according to J. B. Richter, a soln. of sodium sulphate and potassium chloride at ordinary temp. deposits potassium sulphate, and at −20°, sodium sulphate. Constantini also showed that a mixture of alum and sodium chloride gives crystals of sodium sulphate at freezing temp.; and C. F. S. Hahnemann observed the same result with a sat. soln. of calcium sulphate and sodium chloride. Sodium sulphate also separates when a mixed soln. of sodium chloride and ferrous sulphate or of sodium nitrate and ammonium sulphate[11] is

cooled. A. J. Balard also showed that Glauber's salt may be obtained by double decomposition from a mixed soln. of magnesium sulphate and sodium chloride in the cold, the reaction seems to proceed: $MgSO_{4aq}+2NaCl_{aq}=MgCl_{2aq}+Na_2SO_{4aq}$. Accordingly, the *sel mixtes* deposited from the mother liquid from sea-water, and other brines, yield crystals of Glauber's salt when a soln. is cooled below 0°. The cooling may be done artificially as in the works at the mouth of the Rhone, or naturally as at Stassfurt during the winter months.

The residue remaining after the leaching of crude carnallite is dissolved in water—generally the heaps of residue are lixiviated by hot water and the soln. is caught in a trench at the bottom of the heap. The composition of the liquor is adjusted until the mol. proportion of $NaCl : MgSO_4$ is approximately 2 : 1. The soln. is evaporated until its sp. gr. is 1·269 at 33°. The liquor is clarified by settling, and run into large shallow wooden tanks 100×100 ft. sq. and 8 in deep, supported above the ground. These tanks are exposed in the open to the cold of a winter's night, and the mother liquor run off in the morning before it is warm again. A cubic metre of soln. may yield 150–180 kilograms of crystals. In summer the tanks are kept filled with a soln. of brine.

Sodium sulphate is formed as an intermediate stage in the conversion of sodium chloride into carbonate by Leblanc's process when it is obtained by heating a mixture of salt and sulphuric acid. *Nitre cake*, a mixture of normal and acid sodium sulphate with some free acid, is a by-product in the manufacture of nitric acid by the action of sulphuric acid on nitre; any acid sulphate present, $NaHSO_4$, is converted to normal sulphate by roasting with sodium chloride.[12] Sodium sulphate is a by-product in many other chemical operations—*e.g.* in working up kelp liquors as a preliminary to the treatment for iodine; in roasting pyrites-cinders with salt in the extraction of copper (where the resulting sodium sulphate has not been successfully utilized); in the manufacture of ammonium chloride by subliming a mixture of ammonium sulphate with common salt; in making mercuric chloride by subliming a mixture of mercuric sulphate and common salt; in the amalgamation process for extracting silver; in the manufacture of aluminium chloride from common salt and alum; in purifying oils by means of sulphuric acid and caustic lye; in the neutralization of resorcine, alizarine, where alkali fusions have to be neutralized with acid; in the Stassfurt salt industry; etc. Although sulphur dioxide alone does not itself decompose sodium chloride, yet, if mixed with air and steam, sulphur dioxide will completely convert sodium chloride into the sulphate. The favourable temp. lies between 400° and 450°, as in J. Hargreaves and T. Robinson's[13] process for making salt-cake: $4NaCl+2SO_2+O_2+2H_2O=2Na_2SO_4+4HCl$—ferric or cupric oxide acts as catalytic agent. The hydrogen chloride is condensed from the escaping gases in the usual manner. It will be observed that in Hargreaves' process the manufacture of sulphuric acid is a preliminary to the conversion of sodium chloride into sulphate. The process has been worked successfully in many factories; the disadvantage is the length of time required for the conversion. The product is a little more pure than that obtained by the sulphuric acid process. E. Thomas, M. Dellisse, and M. Boucard also proposed to make sodium sulphate by roasting a mixture of pyrites and sodium chloride in a stream of air, and leaching the soluble salt from the product. This idea is quite old; it was suggested by J. J. Berzelius in 1836, and it is the basis of W. Longmaid's patents in 1842–4. The Griesheim Chemische Fabrik patented the calcination of the sulphide residue from the black ash process with the acid sulphate residue from the nitric acid process: $CaS+2NaHSO_4=H_2S+Na_2SO_4$. The latter is readily obtained by crystallization of the aq. extract of the product. Numerous other proposals have been made for the manufacture of sodium sulphate cheaply on a large scale. Many of these are described in R. Wagner's *Regesten der Sodafabrikation* (Leipzig, 1866), or in G. Lunge's *The Manufacture of Sulphuric Acid and Alkali* (London, 1913). R. de Luca,[14] for example, suggested heating an intimate mixture of the magnesium sulphate found in several parts of Spain with sodium chloride or nitrate in a current of steam at 210° whereby hydrogen chloride, magnesium oxide, and sodium sulphate

are formed. The latter can be isolated by extraction with water. The history of the process really dates back to Earl of Dundonald's patent in 1795. The reaction with gypsum and salt, though several times patented, does not occur unless it be conducted in the presence of siliceous materials, since J. B. Trommsdorff has shown that no decomposition occurs if gypsum and common salt be melted together, although J. Nicklès states that if pyrosulphate be present the reaction does take place.

H. Bauer[15] melted an intimate mixture of cryolite and gypsum and extracted sodium sulphate by leaching the mass with water : $2AlF_3.3NaF+3CaSO_4=3Na_2SO_4+3CaF_2+2AlF_3$. The formation of sodium sulphate by heating sodium chloride with aluminium sulphate or alum, with the direct object of preparing alumina : $Al_2(SO_4)_3+6NaCl+3H_2O=3Na_2SO_4+Al_2O_3+6HCl$, or aluminium chloride : $Al_2(SO_4)_3+6NaCl=3Na_2SO_4+2AlCl_3$, is old. The process is mentioned in the Earl of Dundonald's[16] patent, 1795, and the reaction has been examined by many early workers. C. F. S. Hahnemann, in 1789, mentioned the formation of sodium sulphate by roasting ferrous sulphate and other iron salts with sodium chloride, and the reaction has been examined by many others. W. Garroway patented the heating of a mixture of ferric or aluminium sulphate with sodium nitrate ; the gases evolved were to be used in the manufacture of sulphuric acid by the chamber process, sodium sulphate was to be removed by leaching the product, and the insoluble residue was to be used for making paint. The use of mixtures of sodium chloride with copper sulphate (J. Wilson,[17] 1838 ; W. Hunt, 1840), zinc sulphate (W. Hunt, 1840 ; S. Boulton, 1852), manganese sulphate (J. Barrow, 1856), and lead sulphate (F. Margueritte, 1855) have also been patented as processes for converting sodium chloride into sulphate. A very small proportion of the number of patents which have been issued have had any influence on industrial developments. Many patents are born, most are still-born, and but few live.

The preparation of potassium sulphate.—In the older method of preparing nitric acid by treating potassium nitrate with sulphuric acid, potassium sulphate was obtained as a by-product. An impure form of this salt containing 75 to 85 per cent. of K_2SO_4 and 9 to 21 per cent. Na_2SO_4, etc., and known as *plate-sulphate*,[18] is separated during the conc. of kelp-liquors. Crude potashes prepared from plant ashes also contain some potassium sulphate which can be readily separated by crystallization from the carbonate on account of its comparatively low solubility. Some also is obtained as a by-product in working up beet-root vinasse. In the manufacture of potassium carbonate from the chloride, by Leblanc's process, potassium sulphate is formed in the first stage of the operation by the action of sulphuric acid on the chloride. Several of the obsolete methods used for converting sodium chloride into sulphate, have also been patented for the analogous conversion of potassium chloride. By far the largest quantity of the potassium sulphate in commerce is either obtained from kainite of the Stassfurt deposits, or else obtained by the action of sulphuric acid on potassium chloride likewise derived from the same deposits. Quite a number of processes have been patented for extracting potassium sulphate either from kainite, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$, or from mixtures of kieserite, $MgSO_4.H_2O$, with potassium chloride, or carnallite, $KCl.MgCl_2.6H_2O$, so as to form a kind of artificial schönite, $K_2SO_4.MgSO_4.6H_2O$, of a similar composition to natural schönite :

If a hot soln. of two mols. of kieserite and one mol. of potassium chloride be cooled, the resulting schönite and carnallite can be separated by crystallization for a crop of crystals of schönite separate out immediately : $2MgSO_{4aq}+2KCl_{aq}=K_2SO_4.MgSO_{4aq}+MgCl_{2aq}$; or $2MgSO_{4aq}+3KCl_{aq}=K_2SO_4.MgSO_{4aq}+KCl.MgCl_{2aq}$. This process[19] is not profitable ; and it is more usual to prepare a cold sat. soln. of kainite, and use this for extracting fresh kainite at about 80°, the clarified soln. deposits crystals of schönite on cooling ; and the mother liquid, rich in magnesium, sodium, and potassium chlorides, is utilized in the extraction of potassium chloride from carnallite. In Precht's process, the kainite is treated with water of previous liquors at 120°–145° with a steam press. of from 2–7 atm. By a mechanical arrangement of stirrers, the double salt, $K_2SO_4.2MgSO_4.H_2O$, which is formed can be separated from the residual rock-salt and from the soln. The double salt so formed

is converted into schönite by agitation with a small quantity of water. K. Kubierschky found that when solid potassium chloride is added to a soln. of kieserite of the right conc., at 25°, a precipitate of potassium sulphate, not schönite, is obtained.

Artificial schönite—also called *Kalimagnesia*—readily separates into potassium sulphate, etc.

H. Precht separates potassium sulphate from schönite by running a hot sat. soln. of schönite upon dry potassium chloride: $K_2SO_4.MgSO_4+3KCl=2K_2SO_4+KCl.MgCl_2$. Part of the schönite remains unconverted, so that in practice twice the theoretical amount of chloride is required. The less soluble potassium sulphate crystallizes from the soln. and it is separated by a centrifugal machine. If the temp. falls below 40°, potassium chloride separates out, and this is followed by schönite, and then by carnallite. The reaction is also effected by digesting crystallized schönite with a cold sat. soln. of potassium chloride. A number of other processes have been proposed for breaking down the schönite—*e.g.* by the action of superheated steam on a mixture of schönite with finely crushed coal, by heating schönite itself with coal: $2K_2Mg(SO_4)_2+C=2K_2SO_4+2MgO+2SO_2+CO_2$; by ignition with ferric oxide; by heating a mixture of schönite with silica or a silicate in steam; etc.

In the leaching processes, large volumes of liquid have to be handled, and the mother liquors contain large amounts of salts in soln.; much potassium chloride is rendered less useful since these liquors are boiled down and utilized in other ways—principally as fertilizers. The mother liquors also yield rubidium alum. The cost of the operation, small as it is, does not enable potassium sulphate to be prepared of a sufficient degree of purity to enable it to displace the potassium chloride and sulphuric acid process which can be made to yield almost the theoretical amount of sulphate. Consequently, most of the schönite—natural or artificial—is sold as a fertilizer.

The alkali sulphates can also be made by neutralizing, say, a soln. of 5 grms. of sulphuric acid in 30 c.c. of water with the alkali hydroxide or carbonate, and evaporating the soln. until crystals begin to form. The process is not economical except on a small scale. It is used mainly for lithium, rubidium, and cæsium sulphates. H. Erdmann [20] treated a hot soln. of crude rubidium iron alum with milk of lime made from purified lime, and filtered the liquid from the excess of lime, calcium sulphate, and ferric hydroxide, by suction. The small amount of lime in soln. is precipitated by adding rubidium carbonate. The filtrate is neutralized with sulphuric acid, and evaporated to the point of crystallization.

According to P. Heinrich, if conc. sulphuric acid be dropped on to solid potassium hydroxide in darkness, a flash of light appears when the acid touches the alkali; and, according to L. Troost, metallic lithium inflames in contact with conc. sulphuric acid, while, according to R. Bunsen and A. Matthiessen,[21] the metal is but slowly attacked by the cold acid.

The properties of the alkali sulphates.—Lithium sulphate can be prepared as the anhydrous and hydrated as monohydrated lithium sulphate, $Li_2SO_4.H_2O$; and sodium sulphate as the anhydrous salt, as heptahydrated sodium sulphate, $NaSO_4.7H_2O$; and decahydrated sodium sulphate, $Na_2SO_4.10H_2O$. Mono- and trihydrated sodium salts have been reported—the former by J. Thomsen,[22] the latter by H. Rose—but L. C. de Coppet has questioned the two last-named hydrates.

The **crystals** of anhydrous lithium sulphate which separate from the molten mass are pseudo-octahedra belonging to the monoclinic system with axial ratios: $a:b:c=1\cdot0038:1:1\cdot380$; $\beta=92°\ 8'$. According to G. Wyrouboff,[23] above 500°, the crystals of lithium sulphate belong to the cubic system, and at about 500°, they pass into a very labile, feebly doubly-refracting variety; they decompose on further cooling into the pseudo-octahedral variety belonging to the monoclinic system. When the monoclinic crystals are heated, they pass fairly quickly at about 500° into the cubic modification. K. Hüttner and G. Tammann could find only one enantiotropic transformation point at 575° on the cooling curve of lithium sulphate. Lithium sulphate is not isomorphous with the sulphates of the other alkali metals. The monohydrated salt, $Li_2SO_4.H_2O$, forms monoclinic plates with axial ratios: $a:b:c=1\cdot6066:1:0\cdot5633$; $\beta=93°\ 5'$.

Anhydrous sodium sulphate, Na_2SO_4, *thenardite*, forms rhombic bipyramidal crystals [24] with axial ratios: $a:b:c=0.4731:1:0.7996$. When heated to 200°, O. Mügge states that the crystals pass into an isotropic variety and then into a form with negative double refraction. According to G. Wyrouboff, anhydrous sodium sulphate is tetramorphous: (i) The α- form or thenardite is stable below 33°; (ii) the β-form which is monoclinic and is produced when thenardite is heated to about 180°, or when the γ-variety is exposed to the air for a few minutes; (iii) the γ-form is produced when the molten sulphate is cooled; it forms rhombic crystals; and (iv) the δ-form is hexagonal, and can exist only above 500°. The α-variety combines immediately with water at 25°, while the β-form does not hydrate, and only when the β- has passed into the α-form does hydration occur. A. Hantzsch objected to G. Wyrouboff's statement that alcohol precipitates the decahydrated salt from fresh soln. of the α-salt, while the anhydrous salt is precipitated from fresh soln. of the β-salt. The existence of these different varieties of anhydrous sodium sulphate has been suggested as an explanation of certain curious and apparently anomalous facts. For example, L. C. de Coppet found that it is heated strongly when in contact with water at a temp. above which it is known to form no hydrate; and S. U. Pickering and M. Berthelot obtained very variable results for the heat of soln. Thus, the salt prepared below 150°—α-form—has a heat of soln. of 57 Cals., whereas the salt obtained at a higher temp.—β-form—disengages 760 Cals. The heating and cooling curves of sodium sulphate by K. Hüttner and G. Tammann, N. S. Kurnakoff and F. S. Schemtschuschny, and H. E. Boeke show only one transition point between 235° and 253°; and R. Nacken detected a marked change in the optical properties of sodium sulphate above 230°. According to J. C. G. de Marignac,[25] the tetragonal crystals of heptahydrated sodium sulphate, $Na_2SO_4.7H_2O$, have the axial ratio $a:c=1:0.7346$—with positive double refraction; and, according to W. Haidinger, the monoclinic crystals of mirabilite, decahydrated sodium sulphate, $Na_2SO_4.10H_2O$, have the axial ratios $a:b:c=1.1158:1:1.2380$; $\beta=107°\ 45'$—with negative double refraction.

The rhombic bipyramidal crystals of potassium sulphate form an isomorphous group with those of the corresponding salts of rubidium and cæsium. The axial ratios and mol. vol. are indicated in Table XXXVI; the axial ratios and topical parameters of the three last-named salts were determined by A. E. H. Tutton.[26]

TABLE XXXVI.—SOME CRYSTALLOGRAPHIC CONSTANTS OF THE ALKALI SULPHATES.

	Rhombic $a:b:c$	$a.b.c.$	Sp. gr. D	Mol. wt. M	$a.b.c.\frac{D}{M}$	Ratio.
Li_2SO_4	1·0038 : 1 : 1·3800	1·3852	2·221	110·1	0·002885	[4]
Na_2SO_4	0·4731 : 1 : 0·7996	0·3673	2·673	142·2	0·006482	[9]
K_2SO_4	0·5727 : 1 : 0·7418	0·4248	2·666	174·4	0·006496	9 or 27
Rb_2SO_4	0·5723 : 1 : 0·7485	0·4284	3·615	267·1	0·005798	8 or 24
Cs_2SO_4	0·5712 : 1 : 0·7531	0·4303	4·246	361·9	0·005048	7 or 21

The replacement of potassium by rubidium, or rubidium by cæsium, produces a regular increase in the dimensions of the crystal, and the same regularities occur in the optical properties. The same regularities do not occur with sodium and lithium. A. Ogg and F. L. Hopwood have calculated the lengths of the sides and the volume of the unit rhomb of the crystals potassium, rubidium, and cæsium sulphates from data furnished by the X-ray spectrometer; they find

	Lengths of sides of unit rhomb cm. a.	b.	c.	Volume c.c.
K_2SO_4	5.731×10^{-8}	10.00×10^{-8}	7.424×10^{-8}	425.78×10^{-24}
Rb_2SO_4	5·949	10·394	7·781	486·14
Cs_2SO_4	6·218	10·884	8·198	554·88

There are four mols. in the elementary cell.

According to E. Mallard,[27] the rhombic crystals of potassium sulphate undergo a sudden change at 600° and become hexagonal with negative double refraction; H. le Chatelier gives 580° as the transformation temp. on a heating curve, and 530° on a cooling curve. N. S. Kurnakoff and S. F. Schemtschuschny, and K. Hüttner, and G. Tammann found the change occurs between 587° and 610°: B. Karandéeff, at 599°. The latter also find rubidium sulphate undergoes a similar transformation at about 657°. It is not merely by chance, says O. Mügge, that the majority of substances hitherto examined on a rising temp. approach a higher symmetry, or reach it, as in the case of aragonite, glaserite, nitre, silver iodide, and cryolite. Sulphur and mercury iodide pass gradually from a most highly differentiated crystalline state into the amorphous fluid state in so far as they can do so without decomposition.

The crystals of potassium and sodium sulphates exhibit triboluminescence and crystalloluminescence.[28] According to G. Meslin, the crystals of both salts are diamagnetic.[29] W. G. Hankel has studied the pyroelectrical phenomenon exhibited by the crystals.

The best representative values of the **specific gravities** and **molecular volumes** of the anhydrous alkali sulphates are indicated in Table XXXVII. The sp. gr.

TABLE XXXVII.—PARAMETERS OF THE ALKALI SULPHATES.

	Sp. gr.	Mol. vol.	Topical parameters. χ	ψ	ω	Double refraction.
$LiSO_4$	2·221	49·6	—	—	—	—feeble
Na_2SO_4	2·673	141·10	2·4540	5·1860	4·1470	+
K_2SO_4	2·666	64·91	3·8810	3·8574	4·9964	+
Rb_2SO_4	3·615	73·34	4·0304	4·0039	5·2366	+feeble
Cs_2SO_4	4·246	84·58	4·2187	4·1849	5·5175	—feeble

of anhydrous lithium sulphate, Li_2SO_4, determined by W. Spring,[30] is 2·228 (16°); by G. Wyrouboff, 2·221; and by S. Kremers, 2·210 (3·9°); and at a temp., $\theta°$, between 800° and 1000°, E. Brunner gives $1·981-0·0039(\theta-900)$. For the sp. gr. of hydrated lithium sulphate, $Li_2SO_4.H_2O$, L. Troost gives 2·02; and O. Pettersson, 2·052 (21°) and 2·056–2·066 (20°). The reported sp. gr. of sodium sulphate, Na_2SO_4, range from E. Filhol's 2·629 to H. G. F. Schröder's 2·7; P. A. Favre and C. A. Valson's value is 2·681 (20·5°); H. G. F. Schröder's, 2·693 (3·9°); G. Quincke's, 2·66 (0°) and 2·104 at the m.p.; P. Kremers, 2·656 when crystallized at 60°–70°, 2·679 when crystallized at 100° and sulphate which had been fused, 2·6313; and E. Brunner at $\theta°$ between 800° and 1000° gives $2·065-0·00045(\theta-900)$. O. Pettersson gives 1·485 (19°), and 1·492 (20°). The reported sp. gr. of decahydrated sodium sulphate, $Na_2SO_4.10H_2O$, range from F. Stolba's 1·460 to E. Filhol's 1·52; L. Playfair and J. P. Joule's value is 1·469 (3·90°); and P. A. Favre and C. A. Valson, 1·455 (26·5°). The published values of the sp. gr. of potassium sulphate range from G. Karsten's 2·6232 to A. E. H. Tutton's 2·6633 (20°); F. Stolba's 2·645 (16°); P. A. Favre and C. A. Valson's 2·653 (21·8°); and L. Playfair and J. P. Joule's 2·656 (319°). The reported values for rubidium sulphate are 3·640 (16·8°) by O. Pettersson; 4·250 (16°) by W. Spring; and 3·6113 (20°) by A. E. H. Tutton. For cæsium sulphate, A. E. H. Tutton gives 4·2434 (20°); O. Pettersson, 4·105 (19·2°); and W. Spring, 4·250 (16°). F. M. Jäger's values for the sp. gr. of the molten alkali sulphates are indicated in Table XXXVIII. For lithium, the sp. gr. D at $\theta°$, water at 4° unity, is $D=2·008-0·000407(\theta-850)$; sodium sulphate, $D=2·061-0·000483(\theta-900)$; potassium sulphate, $D=1·872-0·0005449(\theta-1100)$; rubidium sulphate, $D=2·562-0·000665(\theta-1050)$; and cæsium sulphate, $D=3·034-0·000711(\theta-1040)-0·000000494(\theta-1040)^2$. E. Brunner's value for

sodium sulphate is $D=0·065-0·00045(\theta-900)$. For the effect of press. on the sp. gr. of potassium sulphate, *vide* the alkali chlorides.

The **capillary constants** [31] of molten sodium and potassium sulphate are respectively $a^2=17·64$ and 17·25 sq. mm.; while the **surface tensions** are respectively 182 and 177·7 dynes per cm. F. M. Jäger's values for the surface tension (dynes per cm.), sp. gr., and mol. **surface energy** (ergs per sq. cm.) of molten alkali sulphates are indicated in Table XXXVIII.

TABLE XXXVIII.—THE SPECIFIC GRAVITIES AND SURFACE TENSIONS OF THE MOLTEN ALKALI SULPHATES.

	Temp.	Surface tension.	Sp. gr.	Mol. surface energy.	Temp. coeff. per degree.
Li_2SO_4	860°	223·8	2·004	3231	0·50
	1214°	200·3	1·860	3039	0·50
Na_2SO_4	900°	194·8	2·061	3295	0·30
	1077°	184·7	1·971	3199	0·30
K_2SO_4	1070·2°	143·7	1·888	2935	0·90
	1656°	106·8	1·569	2468	0·90
Rb_2SO_4	1086°	132·5	2·538	2953	1·92
	1545°	108·9	2·233	2643	0·27
Cs_2SO_4	1036°	111·3	3·037	2694	1·91
	1530°	83·0	2·566	2248	0·43

A. E. H. Tutton [32] gives for the **coefficients of thermal expansion** of the crystals, at 0°, in the directions of the a, b, and c axes :

	a	b	c
Potassium sulphate	0·00003616	0·00003225	0·00003634
Rubidium sulphate	3637	3214	3463
Cæsium sulphate	3385	3195	3590

The best representative values for the **melting points** of the anhydrous alkali sulphates [33] are

	Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4
M.p.	859°	880°	1074°	1074°	1019°

The values for lithium sulphate range from T. Carnelley's 818° ± 2° to K. Hüttner and G. Tammann's 859°; for sodium sulphate, from V. Meyer and W. Riddle's 861° to K. Hüttner and G. Tammann's 897°; for potassium sulphate from H. le Chatelier's 1015° to V. Meyer and W. Riddle's 1078°; for rubidium sulphate, K. Hüttner and G. Tammann give 1074°, and for cæsium sulphate, 1019°. According to G. Tammann, the change in vol. dv on melting Glauber's salt is $dv=0·0037-0·000008p$, when the press. is p; and the effect of press. on the m.p. θ is $\theta=32·6+0·000507p-0·00000055p^2$. E. Cohen gave for the **latent heat of fusion,** 48 cals. per gram, or 16500 cals. per mol.

Sodium or potassium sulphate volatilizes in a platinum crucible at the temp. of a powerful blast-gas flame, and if but partially volatilized, in the hottest part of a Bunsen's flame, the residue has an alkaline reaction. According to R. Bunsen,[34] potassium sulphate volatilizes 15·04 times as rapidly as sodium chloride, and 10 times as rapidly according to T. H. Norton and D. M. Roth. The corresponding numbers for potassium sulphate are 7·89 and 6·73. D. D. Jackson and J. J. Morgan found the **vapour pressure** of potassium sulphate to be 0·4 mm. of mercury at 1130°. G. P. Baxter and J. E. Lansing measured the vap. press. of crystals of hydrated sodium sulphate. According to A. Schüller,[35] the **specific heat** of sodium sulphate is 0·2293 (28°–57°); 0·23115 (15°–98°), according to H. V. Regnault; and 0·227 (13°–45°), according to H. Kopp. For potassium sulphate, H. V. Regnault gives 0·19011 (15°–98°); and H. Kopp, 0·196 (13°–45°).

The **heats of formation** [36] of anhydrous alkali sulphates from their elements is

	Li_2SO_4	Na_2SO_4	K_2SO_4	Rb_2SO_4	Cs_2SO_4
Heat formation	342	328·6	244·6	344·7	349·8 Cals.
Heat soln.	6·05	0·5	−7·4	−6·7	−5·0 Cals.

The heat of formation in dil. aq. soln. $2LiOHaq+H_2SO_4aq=31·29$ Cals.; for sodium sulphate, 31·38 Cals.; for normal soln. of potassium sulphate, 31·29 Cals. The **heat of solution** of anhydrous lithium sulphate is 6·05 Cals. (J. Thomsen) and 6·05 Cals. (S. U. Pickering); for sodium sulphate is $400H_2O$, J. Thomsen gives 0·46 Cals.. and M. Berthelot and L. Ilsovay de Nagy Ilsova, give for the heat of soln. Q of sodium sulphate in $100H_2O$ at $\theta°$, the interplation formula $Q=0·44+0·0526(\theta-15)$ Cals. J. Thomsen gives −6·38 Cals. for the heat of soln. of potassium sulphate in $400H_2O$; and for $100H_2O$ at 15°, M. Berthelot and L. Ilsovay de Nagy Ilsova, −6·158 Cals. According to S. U. Pickering, the heat of soln. of potassium sulphate in $400H_2O$ at 3° is −7·997 Cals.; at 10°, −7·301 Cals.; at 20°, 6·41 Cals. R. de Forcrand gives for the heat of soln. of rubidium sulphate, −6·66 Cals. at 15°; and for cæsium sulphate, −4·97 Cals; the heat of formation of hydrated lithium sulphate: $Li_2SO_4+H_2O=2·64$ Cals. J. Thomsen gives the heat of formation of decahydrated sodium sulphate: $Na_2SO_4+10H_2O=19·22$ Cals., or, according to M. Berthelot, 18·64 Cals. The heat of soln. of hydrated lithium sulphate, $Li_2SO_4.H_2O$, is 3·4 Cals.; for decahydrated sodium sulphate, $Na_2SO_4.10H_2O$, in $400H_2O$, J. Thomsen gives −18·8 Cals.; and M. Berthelot, with 900 to $1800H_2O$, −18·1 Cals. J. Thomsen found for the heat of dilution of sodium sulphate soln. containing n mols. of water, $n=0$, 0 Cal.; $n=100$, −0·665 Cal.; $n=200$, −1·13 Cals.; $n=400$, −1·38 Cals.; and $n=600$, −1·48 Cals. M. Berthelot pointed out that his value for the heat of soln. of sodium sulphate, $Na_2SO_4+Aq=0·78$ Cal., differs from P. A. Favre's value 0·17 Cal. far too much to come within the range of experimental error, and he came to the conclusion that these and similar discrepancies with magnesium sulphate, $MgSO_4.H_2O+Aq=13·3$ Cals. (J. Thomsen), and 10·986 Cals. (M. Berthelot), etc., are best explained by assuming that these salts exist in at least two modifications. Previously fused sodium sulphate has a higher value than the unfused salt. S. U. Pickering found that previously fused sodium sulphate has a mol. ht. of dissolution of 61–68 cals., and the unfused salt 47–50 cals., and he infers that the one form is converted into the other at about 200°. It has not been tested whether the explanation is not due to a partial decomposition of the salt during fusion as in the analogous case of sodium carbonate.

The **water solubilities** of the alkali sulphates, expressed in grams of anhydrous salt per 100 grms. of soln., are

	0°	10°	20°	40°	60°	80°	100°
Li_2SO_4 . . .	26·1	25·9	25·5	24·7	24·2	23·5	23·0
Na_2SO_4 . . .	4·76	8·3	16·3	32·8	31·2	30·4	29·8
K_2SO_4 . . .	6·85	8·44	10·00	12·86	15·38	17·63	19·41
Rb_2SO_4 . . .	27·3	29·9	32·5	36·9	40·3	42·9	45·0
Cs_2SO_4 . . .	62·6	63·4	64·1	65·5	66·7	67·8	68·8

The solubility data for lithium sulphate are by P. Kremers [37] and A. Étard; according to H. Lescœur, the monohydrated salt, $Li_2SO_4.H_2O$, is the solid phase from 0° to over 100°. There is a maximum in the solubility curve of 26·5 at −5°; 18·4 at −20°.

A. Étard gives the percentage solubility S of lithium sulphate at $\theta°$ between −20° and −10·5° as $S=18·5+0·8421\theta$, and between −10·5° and 100°, by $S=26·5-0·0241\theta$. T. W. Richards and V. Yngve found the solubility S of sodium sulphate in grms. of Na_2SO_4 per 100 grms. of water at $\theta°$ between 15° and 25° is $\log S=0·659970+0·0296388\theta+0·0000688925\theta^2$, and the solubility of this salt has been suggested as a means of measuring temp. Data for sodium sulphate have been obtained by J. L. Gay Lussac, L. C. de Coppet, H. Löwel, Earl of Berkeley, and T. W. Richards and R. C. Wells; data over 100° have been obtained by

A. Étard, and by W. A. Tilden and W. A. Shenstone. The eutectic temp. with 3·85 per cent. of Na_2SO_4 is at $-1·2°$; the solid phase up to 32·383° is decahydrated sodium sulphate, $Na_2SO_4.10H_2O$: and above that temp., the anhydrous salt is the solid phase with a solubility 29·5 at 120°; 29·6 at 140°; 20·40 at 160°; 31·4 at 180°; and 31·7 at 230°; A. Étard gives 29·90 at 190°; 30·80 at 240°; and 17·80 at 320°. The metastable heptahydrated sodium sulphate, $Na_2SO_4.7H_2O$, has its eutectic temp. with 12·7 per cent. Na_2SO_4 at $-3·55°$; and H. Löwel's data for the solubility, expressed in grams of anhydrous salt per 100 grms. of soln. with the solid phase $Na_2SO_4.7H_2O$, and $Na_2SO_4.10H_2O$, are:

	0°	5°	10°	15°	20°	24·4°
Heptahydrated salt .	16·3	19·4	23·1	27·0	30·6	34·1
Decahydrated salt .	4·76	6·0	8·3	11·8	16·3	21·9 (25°)

Hence, in accord with the general rule, the solubility for the labile phase, $Na_2SO_4.7H_2O$, is greater than for the stable phase, $Na_2SO_4.10H_2O$. The transition temp. of the heptahydrated salt to anhydrous sodium sulphate is 24·4. J. P. Wuite's solubility curves are illustrated in the chapter on solutions. J. Block, and G. Tammann have studied the effect of press. on the transition temp. The data for potassium sulphate are by L. C. de Coppet, J. L. Andreæ, Earl of Berkeley, and J. E. Trevor. According to G. Bruni, the eutectic temp. with 6·54 per cent. of potassium sulphate, is $-1·55°$, and, according to W. A. Tilden and W. A. Shenstone, the solubility at 120° is 20·9; at 143°, 22·4; and at 170°, 24·7 per cent. A. Étard says the solubility between 175° and 220° is virtually constant with 24·5 per cent. K_2SO_4. For the solubility curve of potassium sulphate between 0° and 160°, A. Étard gives $S=7·5+0·107\theta$; and C. Blarez between 0° and 30°, $S=8·5+0·12\theta$. A. E. Nordenskjöld also gives $\log S=1·1061+0·008117\theta-0·000032450\theta^2$; and J. L. Andreæ, $S=9·219+0·19304(\theta-10)-0·0003083(\theta-10)^2$. The data for rubidium and cæsium sulphates are by A. Étard, and Earl of Berkeley—at 102·4° the solubility of rubidium sulphate is 45·2 per cent., and of cæsium sulphate at 108·6°, 69·2 per cent.

C. Blarez [38] found the solubility of potassium sulphate to be depressed by the presence of potassium chloride, bromide, or iodide to such an extent that as much potassium sulphate is precipitated from the sat. soln. as is eq. to the potassium added as halide. A. Seidell also found the solubility of sodium sulphate to be depressed with increasing proportions of sodium chloride in the soln., sodium sulphate is almost insoluble in soln. with 35·5 grms. of sodium chloride per 100 grms. of water. J. von Liebig stated [39] that potassium sulphate does not dissolve in potash-lye of sp. gr. 1·35; A. Stromeyer also found that potassium sulphate dissolves but sparingly in soln. of potassium acetate. Of all the salts of potassium yet tried, the sulphate is the least soluble in aqua ammonia.[40] Thus H. Giraud found that 100 c.c. of soln. containing 0, 15·37, and 31·02 grms. of NH_3 in 100 c.c. of water, dissolved respectively 10·804, 0·828, and 0·042 grms. of potassium sulphate. Potassium sulphate dissolves much more readily in soln. of sodium sulphate, magnesium, or copper sulphate than it does in water alone, due, no doubt, to the formation of double salts.

According to H. Kolbe,[41] lithium sulphate is insoluble in absolute ethyl alcohol, but C. W. G. Kastner found it to be soluble in aq. alcohol, and F. A. H. Schreinemakers and W. A. van Dorp found lithium sulphate to be virtually insoluble in 80 per cent. alcohol, but the solubility increases rapidly as the amount of water increases. The solubility of sodium sulphate in aq. alcohol of different temp. and conc. has been studied by C. A. L. de Bruyn.[42] Sodium sulphate is virtually insoluble in alcohol of greater conc. than about 72 per cent. For example, at 15°, with decahydrated sodium sulphate, per 100 grms. of soln.:

Water	88·7	85·1	78·6	60·0	41·1	28·0
Alcohol	0	8·6	18·9	39·5	58·8	72·0
Na_2SO_4	11·3	6·3	2·9	0·5	0·1	0·0

With certain conc., the soln. separates into two layers thus, at 25°, the upper layer has $H_2O : C_2H_5OH : Na_2SO_4$ in grms. per cent., 66·5 : 27·3 : 6·2, and the lower layer, 67·4 : 5·1 : 27·5 ; at 45°, the upper layer has 66 : 24 : 10, and the lower layer, 68·6 : 10·1 : 21·3. A. Gérardin and H. Schiff found with 10 per cent. alcohol, at 15°, 100 grms. of a sat. soln. contained 3·9 grms. of potassium sulphate, 20 per cent. alcohol, 1·46 grms. ; 30 per cent., 0·56 ; and 40 per cent., 0·21. While 100 grms. of alcohol of sp. gr. 0·939, at 60°, dissolved 0·92 grm. of potassium sulphate, only 0·16 grm. was dissolved at 40°. According to C. E. Linebarger, 100 grms. of 24·2 per cent *propyl alcohol* dissolve 1·99 per cent. of sodium sulphate ; and 62 per cent. propyl alcohol, 0·38 per cent. sodium sulphate. V. Rothmund and N. T. M. Wilsmore found *acetic acid* dissolved 4·2 grms. Na_2SO_4, and 115·4 grms. K_2SO_4 per litre at 25° ; and 128·58 grms. Na_2SO_4 and 82·7 grms. K_2SO_4. Similarly with *phenol*, 3·01 grms. C_6H_5OH and 115·0 grms. K_2SO_4 were dissolved per litre ; and 46·82 grms. C_6H_5OH and 93·8 grms. K_2SO_4. According to A. Köhler, 100 grms. of a sat. soln. containing 52 grms. of *sugar* hold 9·6 grms. of sodium sulphate in soln. ; and 100 grms. of a sat. soln. containing 66·74 grms. of sugar hold 3·18 grms. of potassium sulphate in soln. A. Vogel found 100 grms. *glycerol* of sp. gr. 1·255 dissolve 1·316 grms. of potassium sulphate at ordinary temp. ; and at ordinary temp., W. F. O. de Coninck says that *glycol* dissolves 3·0 to 3·2 per cent. of cæsium sulphate.

According to V. Rothmund's experiments [43] on *reciprocal solubility*, if the solubility of a substance *A* is diminished (or increased) by the addition of another substance *B*, then the solubility of *B*, in turn, will be decreased (or increased) by the addition of *A*. R. Löwenherz found that the solubility of anhydrous sodium carbonate at 32° is considerably depressed by the addition of urea to the soln., and the solubility of the decahydrate is slightly increased in presence of urea. Accordingly, it might be argued from V. Rothmund's rule, that the solubility of urea will be increased in soln. of the decahydrate, and decreased in solns. of the anhydrous salt, but C. S. Hudson argues that soln. of the two crystalline forms of sodium sulphate are identical in physical and chemical properties, and hence the solubility of urea cannot be affected in the way predicted by V. Rothmund's reciprocal solubility rule.

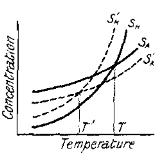

FIG. 42.

In Fig. 42, let the curves S_A and S_H respectively denote the solubilities of an anhydrous salt and one of its hydrates associated with *n* mols. of water. Let *T* be the transition temp. where the vap. press. of a mixture of the two solids is equal to the vap. press. of their common sat. aq. soln. If a foreign solute be added to the soln., the vap. press. is reduced, the transition temp. in the new soln. will be reduced to T', and the solubility curves of the anhydride and its hydrate will cross at T' just as they cross at *T* when the pure solvent is used. Since the transition temp. T' is lower than *T*, it will be necessary for the solubility of at least one of the two solids to be changed by the presence of the foreign substance. In that case it can be shown that (1) the solubility of the anhydride S_A which forms a hydrate in soln. will be changed to S_A' ; (2) the solubility S_H of the hydrate will likewise be increased to S_H' ; (3) when a number of hydrates are formed in aq. soln., the solubility of the hydrate which has the greatest proportion of water will be increased ; and (4) when a number of hydrates are formed in aq. soln., the solubility of the hydrate, which has less water than the hydrate in the solid phase, will be increased, and, conversely, the solubility of those hydrates with more water than is present in the solid phase, will be diminished.

Aq. soln. of lithium sulphate furnish monoclinic plates of **monohydrated lithium sulphate,** $LiSO_4.H_2O$. G. C. A. van Dorp's equilibrium curves are shown in Fig. 44. If a conc. soln. of lithium sulphate be kept boiling for some time, J. W. Retgers [44] says that rhombic needle-like crystals of the anhydrous salt are

formed which have analogous optical properties with the anhydrous salt which has been fused or calcined. The sp. gr. of the hydrated salt is smaller than that of the anhydrous salt, as indicated above. M. Faraday noticed that if the aq. soln. of sodium sulphate be evaporated "considerably beneath the b.p. of the soln." the crystals resemble those of potassium sulphate more than Glauber's salt, and they are anhydrous. W. Haidinger[45] made a similar observation. E. Mitscherlich placed 33° as limiting temp. above which crystals of the anhydrous salt are obtained and below which Glauber's salt is formed. More exact investigations by T. W. Richards and R. C. Wells, and by H. C. Dickenson and E. F. Müller, place the transition temp. at 32·383°±0·001°. This point is so sharply defined and easily reproduced that it has been proposed as a fixed point in thermometry. R. Lowenherz found the transition point to be lowered in the presence of certain foreign materials, thus, J. H. van't Hoff and A. P. Saunders found the presence of sodium chloride lowered the transition point to 18°; and C. Schultz-Sellack stated in 1871 that the anhydrous salt separates at ordinary temp. from strongly alkaline soln. If the crystallization from aq. soln. occurs below 32·383°, crystals of **decahydrated sodium sulphate,** $Na_2SO_4.10H_2O$, are formed. S. Tanatar was able to replace one of the mol. of the water of crystallization by a mol. of hydrogen peroxide of crystallization. S. Tanatar[46] evaporated a soln. of sodium sulphate in 3 per cent. hydrogen peroxide at 50°, and as soon as crystallization commenced, precipitated the sulphate by the addition of alcohol. The crystals contained the eq. of $Na_2SO_4.9H_2O.H_2O_2$, and lost about half the hydrogen peroxide in a week's time.

Soln. of sodium sulphate very readily assume a state of supersaturation or under-cooling by simply lowering the temp. of a warm soln. of sodium sulphate in half its weight of water while the flask is plugged with cotton wool. These soln. have been accordingly largely employed in the study of this phenomenon. The state of supersaturation is upset, and the process of crystallization inaugurated by the introduction of a fragment of solid Glauber's salt, which W. Ostwald estimates should not be smaller than 10^{-9} grms. There is usually enough dust of sodium sulphate crystals in the atm. to start the process of crystallization. Crystals of other unrelated salts will not serve the same purpose. The labile state occurs when the soln. has been cooled below −15°, crystallization then spontaneously occurs without the need for seeding with a crystal of the solid salt.

M. Faraday[47] noted that while a hot conc. soln. of sodium sulphate in a closed vessel may be reduced to the common. temp. without crystallizing, in some circumstances, crystals form in the soln. during cooling, even though the vessel has not been opened or agitated. H. Löwel examined the crystals more carefully. H. Ogden's, M. Faraday's, and J. B. Ziz's analyses make the salt appear $Na_2SO_4.8H_2O$, but when freed from contamination with the decahydrated salt, the crystals are those of **heptahydrated sodium sulphate,** $Na_2SO_4.7H_2O$; and J. C. G. de Marignac showed that they belong to the tetragonal system. H. Schiff found that hot alcohol precipitated the heptahydrated sulphate from under-cooled soln. of sodium sulphate, but cold alcohol precipitates the decahydrated sulphate; and R. Brandes and E. Firnhaber say that the decahydrated sulphate is precipitated from cold sat. soln. H. Löwel prepared heptahydrated sodium sulphate in the following manner:

A soln. of 22 parts of Glauber's salt in 10 parts of hot water is poured into a flask. The liquid is cooled and twice its volume of alcohol at 40°, and sp. gr. 0·835, is poured as a layer over the aq. soln. Crystals of the heptahydrated salt, free from the decahydrated sulphate, are formed as the alcohol mixes with the water. The crystalline product can be freed from the adherent liquid by press.

H. Violette[48] and E. H. von Baumhauer believed that this always occurred at −8°, but L. C. de Coppet showed that with the same soln. it could be produced at temp. between 6° and −13·3°. The vap. press. of the soln. of heptahydrated salt at 20°,

is, according to H. Lescœur, 10 5 mm., while those of the decahydrated salt under the same conditions have a vap. press. 27·8 mm. The heptahydrated salt begins to dehydrate near 27°. The fusion temp. of the decahydrated salt is 32·383°, the same as the transition temp., so also the fusion temp. of the heptahydrated salt is 27°, and this is also the temp. at which the heptahydrated salt becomes anhydrous sodium sulphate—Fig. 2—I. 10. 1. In the absence of traces of the decahydrated salt, the crystals of the heptahydrated salt can be preserved unchanged. If a soln. sat. with respect to the heptahydrated salt and in equilibrium with the solid phase be seeded with the decahydrated salt, some decahydrated sodium sulphate will separate from the soln. on account of the lower solubility of the last-named salt. The soln. will therefore no longer be sat. with respect to the heptahydrated salt, and some will dissolve to be immediately precipitated as decahydrated sulphate. *In this way, all the heptahydrated sulphate will be transformed into the decahydrated sulphate.* Hydrated forms of potassium, rubidium, and cæsium sulphates do not separate from aq. soln. J. Ogier [49] claimed to have made hemihydrated potassium sulphate, $K_2SO_4.\frac{1}{2}H_2O$, or $2K_2SO_4.H_2O$, by crystallizing this salt in the presence of benzylsulphonic acid; and T. J. Pelouze a monohydrated sulphate, $K_2SO_4.H_2O$, by the oxidation of potassium sulphite or hyposulphite. There is, however, insufficient acceptable evidence.

P. Kremers [50] gave the **specific gravity** of a soln. with 6·5 grms. of Li_2SO_4 in 100 grms. of water as 1·05; with 12·5 grms., 1·098; with 15·3 grms., 1·118; with 22·6 grms., 1·167; with 24·4 grms., 1·178; and with 29·4 grms., 1·208. G. T. Gerlach has a table of sp. gr. of soln. of sodium sulphate at 15° for soln. of Na_2SO_4 and $Na_2SO_4.10H_2O$ of different percentages:

Per cent. salt	1	5	10	15	20	25	30
Na_2SO_4	1·0091	1·0457	1·0927	—	—	—	—
$Na_2SO_4.10H_2O$	1·004	1·020	10·40	1·060	1·082	1·103	1·125
K_2SO_4	1·0082	1·0410	1·0750 (9)	—	—	—	—

Data have also been given by H. Schiff, W. Schmidt, H. T. Barnes and A. P. Scott, J. C. G. de Marignac, E. H. Archibald, C. M. Pasca, etc. J. G. MacGregor says the sp. gr. of a soln. with w per cent. of sodium sulphate, is $0·0091267w$ plus the sp. gr. of water at the temp. in question; similarly for soln. with less than 2·5 per cent. potassium sulphate, $0·00816w$. O. Pulvermacher measured the sp. gr. of soln. of potassium sulphate. A 9 per cent. soln. at 20·1° has a sp. gr. 1·0800, according to H. T. Barnes and A. P. Scott.[51] According to H. Erdmann,[52] a soln. of rubidium sulphate sat. at 10° has a sp. gr. 1·2978; and, according to J. Kannonikoff, a 6·14 per cent. soln. of the same salt, at 21·4°, has a sp. gr. 1·0485 (water at 4° unity); while a 4·55 per cent. soln. of cæsium sulphate has a sp. gr. 1·0350 at 19·6°.

F. Braun [53] found the coeff. of **compressibility** of soln. of sodium sulphate of sp. gr. 1·045 is 0·000043; and W. C. Röntgen and J. Schneider give for the mol. compressibility soln. containing a mol. of the anhydrous salt per 700 mols. of water at 18°:

	H_2SO_4	$(NH_4)_2SO_4$	Li_2SO_4	K_2SO_4	Na_2SO_4
Compressibility	0·970	0·853	0·813	0·804	0·803

and for soln. with 1500 mols. of water, H_2SO_4, 0·920; $(NH_4)_2SO_4$, 0·741; and Li_2SO_4, 0·655. V. Schumann measured the compressibility of soln. of lithium and potassium sulphates, and W. Schmidt of sodium sulphate. G. Wertheim, and T. Martini measured the velocity of sound in soln. of sodium sulphate.

J. Holmes and P. J. Sagemann [54] have measured the changes in vol., dv, which occur on mixing x per cent. of one set of molecules in a binary mixture where v is the change in vol., and compared them with the calculated values $dv=x(100-x)K$, where K is a constant evaluated from the observed values for equimolecular mixtures. The following results were obtained:

Mols. of salt per cent.	Expansions, &c, in aq. soln. per 100 mols. of sulphuric acid.							
	K_2SO_4		Na_2SO_4	$(NH_4)_2SO_4$	$MgSO_4$	$ZnSO_4$	$CuSO_4$	$Al_2(SO_4)_3$
	Obs.	Calc.						
88·9	139	155	129	114	78	55	48	57
75·0	279	295	261	232	159	115	91	126
50·0	394	—	368	321	226	160	130	196
25·0	269	295	259	207	165	122	100	186
11·1	137	155	126	97	85	61	51	113

According to J. Wagner, and O. Pulvermacher, the **viscosities** of *N*-, $\frac{1}{2}N$-, $\frac{1}{4}N$-, and $\frac{1}{8}N$-soln. of sodium sulphate, water unity, at 17·6°, are respectively 1·2291, 1·1058, 1·0522, and 1·0235; and for potassium sulphate, 1·1051, 1·0486, 1·0206, and 1·0078 respectively. A. Sprung and R. F. d'Arcy[55] noticed no irregularity in the change of viscosity with the temp. of soln. of sodium sulphate in passing through the region of 33°. The **diffusion coefficient** in pure water at 10° for 1·4*N*-soln. of sodium sulphate is 0·66 sq. cm. per day; and for 1·5*N*-soln. of potassium sulphate, 0·75 sq. cm. per day. The **coefficient of cubical expansion of solutions** of lithium sulphate with 27·5 grms. of the salt per litre is 0·000048 from 0° to 5°, 0·000107 from 5° to 10°, and 0·000366 from 35° to 40°; similarly with soln. with 55 grms. of salt per litre, the numbers are respectively 0·000101, 0·000150, and 0·000370; while with soln. with 110 grms. of salt per litre, the respective numbers are 0·000166, 0·000197, and 0·000367. K. Zepernick and G. Tammann[56] find that the volume of *v* of aq. soln. with 1·72 grms. of sodium sulphate in 10 c.c. of water is at $\theta°$ up to $\theta=150°$, $v=1·0524+0·000868(\theta-110)+0·0000022(\theta-110)^2$; and for soln. with 3·46 grms. per 10 c.c. of water, $v=1·0533+0·000815(\theta-110)+0·0000025(\theta-110)^2$. According to W. W. J. Nicol, the coeff. of cubical expansion of soln. below 34° is 0·000470; and at the transition point it falls to 0·000385. C. Forch found the coeff. of cubical expansion of a soln. of 43·5 grms. of potassium sulphate per litre is 0·000078 between 0° and 5°; 0·000135 between 5° and 10°; and 0·000389 between 35° and 40°. Soln. with 87 grms. of the salt per litre have the corresponding numbers 0·000148, 0·000192, and 0·000402 respectively. W. Spring gives 0·0126447 as the coeff. of cubical expansion of soln. of potassium sulphate.

The **specific heat of solutions**[57] of sodium sulphate falls from 0·997 (12°–15°) for 1·9 per cent. soln., to 0·892 (18°) for 10·8 per cent. soln.; to 0·781 (24°–100°) for 30·3 per cent. soln. Similarly, for 4·6 per cent. soln. of potassium sulphate, the sp. *ht.* is 0·9463 (19°–52°), and for 8·8 per cent. soln., 0·902 (19°–52°). G. Jäger found the **thermal conductivity** of 10 per cent. soln. of sodium and potassium sulphates to be respectively 99·8 and 99·3 (water=100).

According to P. Kremers,[58] **the boiling point** of a sat. soln. of lithium sulphate is 105°, while for sodium sulphate H. Löwel gives 103·17°; and G. J. Mulder, 103·5°. C. *Matignon and F. Meyer found a sat. soln. of sodium sulphate boils at* 102° and contains 2·10 mols. per 1000 grms. of soln. Soln. with 9·5 grms. of Na_2SO_4 per 100 grms. of water boil at 100·5°, according to G. T. Gerlach, and with 46·7 grms. of salt, at 103·2. H. Löwel found that a sat. soln., when boiled becomes covered with a crust of anhydrous sodium sulphate. When the soln. sat. at 50° cools to about 29°, *it deposits the decahydrated salt and its temp. then rises to about 31°.* The b.p. of a sat. soln. of potassium sulphate is 103°, according to P. Kremers, and G. T. Gerlach found a soln. with 7 grms. of salt in 100 grms. of water boiled at 100·5°, and with 31·6 grms. of salt, at 102·1°. The Earl of Berkeley gives for the b.p. of a sat. soln. of rubidium sulphate, 102·4°; and for cæsium sulphate, 108·6°.

G. Tammann[59] obtained 14·6 mm. for the **lowering of the vapour pressure** of

water at 100° by 5·99 grms. of lithium sulphate per 100 grms. of water, and by 30·20 grms., 81·1 mm.; by 5·05 grms. of sodium sulphate, 9·0 mm., and by 42·44 grms., 73·6 mm.: 6·31 grms. of potassium sulphate, 10·1 mm., and 21·22 grms., 32·1 mm.; and 11·58 grms. of rubidium sulphate, 12·7 mm., and 64·95 grms., 70·5 mm. According to H. Lescœur, the **dissociation pressure** of decahydrated sodium sulphate is 3·8 mm. at 0°: 5·2 mm. at 5°; 7·0 mm. at 10°; 19·0 mm. at 25°; and 24·0 mm. at 29°. The vap. press. thus rises with temp. to that of the sat. soln. at the transition point, for E. Cohen found at 28·3°, 30·1°, and 32·6°, the vap. press. of sat. soln. of Na_2SO_4 are respectively 24·07, 26·60, and 30·82 mm.; and for sat. soln. of $Na_2SO_4.10H_2O$, respectively 26·20, 28·03, and 30·82 mm. E. Cohen also measured the vap. press. of sat. soln. at different temp.

According to F. Rüdorff,[60] 20 parts of Glauber's salt with 100 parts of water lowers the temp. 6·8°, *i.e.* from 12·5° to 5·7°; 12 parts of potassium sulphate in 100 of water lower the temp. about 3·3°. The **lowering of the freezing point** of a soln. with 0·30 mol. per litre is 3·87°, and it rises to 5·1° as the conc. falls to 0·01 mol. per litre corresponding with the ionization of the salt into three ions. Similar results were obtained with potassium sulphate.

The **indices of refraction**[61] of crystals of potassium, rubidium, and cæsium sulphates have been measured by A. E. H. Tutton, H. Topsöe, and C. Christiansen. A. E. H. Tutton's values at 18°–20° are:

	C-line.			*D*-line.			*F*-line.		
	α	β	γ	α	β	γ	α	β	γ
K_2SO_4 .	1·4916	1·4928	1·4954	1·4935	1·4947	1·4973	1·4982	1·4995	1·5023
Rb_2SO_4	1·5112	1·5113	1·5124	1·5131	1·5133	1·5144	1·5181	1·5183	1·5194
Cs_2SO_4 .	1·5573	1·5419	1·5657	1·5598	1·5644	1·5662	1·5660	1·5725	1·5725

The index of refraction of lithium sulphate soln., $Li_2SO_4+150H_2O$, is 1·3415; and of $Li_2SO_4+30H_2O$, is 1·3610. J. H. Gladstone and W. Hibbert[62] found the refraction eq. for the *D*-line for 5·75 per cent. soln. of sodium sulphate to be 25·84; for 10·93 per cent. soln., 25·93; for potassium sulphate, 5·43 per cent. the refraction eq. is 32·55; and with 10·44 per cent. soln., 32·41; with 9·42 per cent. rubidium sulphate to be 25·84; for 10·93 per cent. soln., 25·93; for potassium sulphate, 5·43 per cent. the refraction eq. is 32·55; and with 10·44 per cent. soln., 32·41; with 9·42 per cent. rubidium sulphate soln., 38·47; and 15·24 per cent. cæsium sulphate, 47·60. In passing into soln., there is 0·55 percentage increase with potassium sulphate, 1·6 with rubidium sulphate, and −0·5 with cæsium sulphate. O. Pulvermacher also measured this constant for soln. of potassium sulphate. The **magnetic rotation** of the plane of polarized light at 15° is 1·0556 for $Na_2SO_4+21·928H_2O$ soln.; 1·0295 for $Na_2SO_4+59·480H_2O$ soln, thus giving for the mol. rotation a value less than that of water which has the respective values 2·953 and 2·869. W. H. Perkin[63] could find no evidence of ionization in sulphuric acid soln. down to conc. of about 10 per cent. H_2SO_4.

Molten sodium sulphate has a specific conductivity[64] 3680×10^{-8} (mercury unity). The **equivalent conductivities,** λ, of soln. of lithium, sodium, and potassium sulphates[65] with *N*-gram-eq. per litre, are, at 18°:

N	0·0001	0·001	0·01	0·1	1·0
$\frac{1}{2}Li_2SO_4$	—	96·42	86·85	68·16	41·35
$\frac{1}{2}Na_2SO_4$	110·5	106·70	96·80	78·40	50·80
$\frac{1}{2}K_2SO_4$	130·71	126·88	115·80	94·93	71·59

The $\frac{1}{10}N$-soln. of lithium sulphate is about two-thirds ionized. 0·01*N*-soln. of potassium sulphate at 0° are 84·5 per cent. ionized; 0·1*N*-soln., 65·5 per cent.: and 0·2*N*-soln., 59·5 per cent. ionized. G. N. Lewis and G. A. Linhart have measured the degree of ionization of soln. of potassium sulphate calculated from A. A. Noyes and G. K. Falk's determination of the ratio λ/λ_∞ and the value calculated thermodynamically, and found the former to be about 20 per cent. less for soln. with 0·01 mol. per litre. The corresponding numbers at 18° are 83·0, 66·0, and 60·1 per cent.

The **transport number** of the anion of potassium sulphate from about $\frac{1}{8}N$- to N-soln. lies between 0·500–0·506 and the temp. coeff. for the conductivity of 0·01N-soln., 0·0223 (18°–26°); and for sodium sulphate soln., 0·0240 (22°). The potential difference [66] of a normal soln. of sodium sulphate against 10 per cent. H_2SO_4 is −0·148 volt; ordinary commercial nitric acid, −0·677 volt; against 60 per cent. KOH, 0·154 volt; and is inappreciable against 33 per cent. $ZnSO_4$, and a sat. soln. of $CuSO_4$. G. M. J. McKay measured the transport number with mixed soln. of potassium chloride and sulphate. A. Heydweiller found respectively 3·34 and 5·87 for the **dielectric constant** of powdered and compact potassium sulphate; and C. B. Thwing, 6·45 for potassium sulphate.

R. Nacken [67] has investigated the f.p. curve of binary mixtures of lithium and sodium sulphate, and found evidence of the formation of compounds $Li_2SO_4.Na_2SO_4$ melting at 520°, and of $2Li_2SO_4.3Na_2SO_4$; with lithium and potassium sulphate, a maximum in the curve corresponds with the formation of $Li_2SO_4.K_2SO_4$ melting at 716°; R. Nacken and E. Jänecke find evidence of the formation of a compound $3K_2SO_4.Na_2SO_4$ melting at 470° with K_2SO_4 and Na_2SO_4, while above 600° they form a eutectic about 20 per cent. K_2SO_4 melting at 830°. R. Nacken found evidence of the formation of a compound of silver sulphate with lithium sulphate —$2Li_2SO_4.3Ag_2SO_4$—but none with silver sulphate and sodium or potassium sulphate.

Lithium sulphate forms no double salt with barium or strontium sulphate, and in this respect it differs from the other alkali sulphates which form compounds of the types $M''SO_4.3M_2'SO_4$; $M''SO_4.M_2'SO_4$; $2M''SO_4.M_2'SO_4$. For example, $SrSO_4.K_2SO_4$; $SrSO_4 3Na_2SO_4$; etc. H. Müller found no evidence of combination, between lithium and calcium sulphate, but with calcium and sodium sulphates, H. Müller and G. Calcagni and G. Mancini found a maximum in the curve at 949° corresponding with the formation of the compound $3Na_2SO_4.CaSO_4$, the calcium analogue of vanthoffite. With potassium, rubidium, or cæsium, and calcium sulphates, H. Müller found evidence of the formation of $K_2SO_4.2CaSO_4$, melting at 1004°; of $Rb_2SO_4.2CaSO_4$, melting at 1043°; and of $Cs_2SO_4.2CaSO_4$, melting at 959°. The fusion curve of beryllium and potassium sulphates show that tetragonal crystals of $K_2SO_4.2BeSO_4$, melting at 910°, are formed. R. Nacken and A. S. Ginsberg found potassium and magnesium sulphates form a compound, $K_2SO_4.2MgSO_4$, melting at 927°, and corresponding with the mineral *langbeinite*; while with sodium and magnesium sulphate there is evidence of the formation of $3Na_2SO_4.MgSO_4$—vanthoffite—and of $Na_2SO_4.3MgSO_4$. Sodium sulphate was found by H. E. Boeke to give no compound with sodium molybdate, Na_2MoO_4, or with sodium tungstate, Na_2WO_4. E. Groschuff found no evidence of combination between potassium sulphate and chromate. A. Wolters found sodium fluoride and sulphate form a compound $NaF.Na_2SO_4$, melting at 781°; B. Karandéeff likewise obtained a maximum with the compound $KF.K_2SO_4$, melting at 887°, on the f.p. curve of potassium fluoride and sulphate; but neither A. Wolters nor E. Jänecke found any with sodium sulphate and chloride.

Potassium, rubidium, and cæsium sulphates are isomorphous and form a series of mixed crystals. Lithium sulphate is not isomorphous with the other alkali metals, and does not form mixed crystals; it does, however, unite with sodium, potassium, rubidium, cæsium, and ammonium sulphates, forming double salts,[68] of the type $Li_2SO_4.M_2SO_4$, or $MLiSO_4$. Some other double lithium sulphates have been reported—$Li_2SO_4.3Na_2SO_4.12H_2O$, that is, $LiNa_3(SO_4)_2.6H_2O$; $Na_4Li_2(SO_4)_3.9H_2O$, and the corresponding anhydrous potassium salt; and $Na_2Li_8(SO_4)_5.5H_2O$ and $K_2Li_8(SO_4)_5.5H_2O$. A mixed soln. of sodium and potassium sulphates deposits optically uniaxial crystals which have been reported as hexagonal potassium sulphate, but these crystals always contain sodium. J. W. Retgers showed every reason to suppose that a double salt, $NaK_3(SO_4)_2$, or $Na_2SO_4.3K_2SO_4$, corresponding with the mineral *glaserite*, is formed. F. Penny [69] has reported the compound $3K_2SO_4.Na_2SO_4$, or $K_3Na(SO_4)_2$; and J. H. Gladstone, $5K_2SO_4.Na_2SO_4$,

or $K_5Na(SO_4)_3$. H. W. B. Roozeboom's[70] study of the system $Na_2SO_4-MgSO_4-H_2O$ shows the conditions under which astracanite, $Na_2Mg(SO_4)_2.4H_2O$, is formed. There are numerous other double salts—the alums, the double sulphates of the type $K_2M(SO_4)_2.6H_2O$, where M represents an atom of cobalt, copper, nickel, zinc, magnesium, or ferrous iron, etc. R. F. Weinland and J. Alfa[71] prepared fluosulphates, $K_2SO_4.KHSO_4.2HF$, that is, $K_3H_3F_2(SO_4)_2$; E. de Haën, $K_2SO_4.SbF_3$; etc.

Chemical properties of the alkali sulphates.—The alkali sulphates volatilize at a high temp. with a slight decomposition, since J. B. J. D. Boussingault[72] found the residue left after incomplete volatilization reacted alkaline. The sulphates are reduced by hydrogen over 500°, forming a mixture of alkali sulphide, and hydroxide and sulphuric acid. The first action, says M. Berthelot, is probably $K_2SO_4+4H_2=KOH+KSH+3H_2O-0{\cdot}9$ Cal., or $Na_2SO_4+4H_2=3H_2O+NaOH+NaSH+14{\cdot}5$ Cals. The hydrosulphide then decomposes $2KSH=K_2S+H_2S$, and the hydrogen sulphide can react with the alkali: $KOH+H_2S=KSH+H_2O+13{\cdot}4$ Cals. The sulphide can also react with water vapour: $K_2S+H_2O=KHS+KOH+7{\cdot}3$ Cals. The hydrogen sulphide may also decompose into hydrogen and sulphur, and the latter can react with the alkali sulphides: $K_2S+3S=K_2S_4+15{\cdot}4$ Cals. **Carbon**[73] acts only at a high temp., forming alkali sulphide and carbon dioxide.[74] A. Colson says that when heated in an iron pipe, practically no reaction occurs below 950°; but above this temp. the reduction is rapid and uniform: $Na_2SO_4+4C=Na_2S+4CO$. **Carbon monoxide** forms the sulphide and carbon dioxide. **Sulphur dioxide** does not act at a red heat, and **sulphur**[75] at a red heat forms sulphide and sulphur dioxide. Finely divided **iron** at a red heat forms potash, and iron sulphide and oxide and **zinc** forms potassium sulphide and zinc oxide. When heated to redness with **ammonium chloride** it is converted into potassium chloride,[76] but the operation must be repeated a number of times for a complete transformation. **Hydrogen chloride** does not appreciably attack potassium sulphate at 0°, the reaction commences about 100°, and at 360°, the conversion to chloride is incomplete; at a red heat all is converted into chloride.[77] The addition of strong acids to soln. of the sulphates converts them partially into salts of the acid with the liberation of sulphuric acid. Thus, A. B. Prescott showed that 0·7 per cent. of potassium chloride is formed when a gram of potassium sulphate is evaporated to dryness with 4·035 grms. of **hydrochloric acid** containing 1·251 grms. of HCl. Conc. **hydriodic acid** converts soluble sulphates into iodides, with the evolution of hydrogen sulphide.[78] To transform a sulphate to a carbonate, dissolve the salt in a soln. of carbonic acid, and add about 1·5 times its weight of barium carbonate after shaking the mixture, heat it to the b.p., and filter off the soln. of alkali carbonate. E. Brunner[79] found that with fused mixtures of **sodium chloride** and lithium sulphate at 900°, the equilibrium condition is 60 per cent. of $(NaCl+\frac{1}{2}Li_2SO_4)\rightleftharpoons(LiCl+\frac{1}{2}Na_2SO_4)$ 40 per cent.

According to G. S. Butler and H. B. Dunnicliff, dry **alcohol** acts on dry sodium hydrogen sulphate, with the formation of the intermediate sulphate, $Na_3H(SO_4)_2$, or $Na_2SO_4.NaHSO_4$, and the liberation of sulphuric acid, which dissolves in the alcohol, and is subsequently converted partly into ethyl hydrogen sulphate. Prolonged action of alcohol does not extract any further quantity of the acid. Methyl, *n*-butyl, and amyl alcohols also react with sodium hydrogen sulphate, with the formation of the same intermediate sulphate. Dry ethyl alcohol does not decompose dry potassium hydrogen sulphate. Moist alcohol will completely decompose sodium hydrogen sulphate, giving first the intermediate sulphate, $Na_2SO_4.NaHSO_4$ and finally normal sodium sulphate. Sodium sulphate is sparingly soluble in moist alcohol. Alcoholic sulphuric acid reacts with sodium sulphate in the cold (18°), with the formation of an acid sulphate. The amount of the interaction increases with the strength of the alcoholic sulphuric acid employed. When alcoholic sulphuric acid acts on sodium hydrogen sulphate, the intermediate sulphate, $Na_2SO_4.NaHSO_4$, is formed if the strength of the alcoholic sulphuric acid corresponds with 20 per cent. or less. When the alcoholic sulphuric acid has a strength

corresponding with 30 per cent. of sulphuric acid or more, the compound, $Na_2SO_4.2NaHSO_4$, is probably produced; if so, this compound is slowly decomposed by constant extraction with pure, dry ether, and finally yields the compound, $Na_2SO_4.NaHSO_4$. The compound, $Na_2SO_4.NaHSO_4$, is formed when dry sodium sulphate is heated with dry sodium hydrogen sulphate.

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§ 26. Alkali Acid Sulphates ; Alkali Hydrosulphates

Il ne faut pas que l'acide soit simplement mêlé avec le sel neutre, il faut qu'il y ait coherence de l'acide avec les autres parties, qu'il fasse combinaison, et qu'il y en ait une juste quantité ; l'excès d'acide a aussi son point de saturation.—G. F. Rouelle (1754).

In an important *Mémoire sur les sels neutres*, published in 1754, G. F. Rouelle [1] was the first to comment on the formation of crystals of alkali bisulphate, or the alkali hydrogen or acid sulphate by the action of sulphuric acid on the neutral sulphate. He emphasized the fact that *sels acides*, as distinguished from *sels neutres*, are formed by the action of a superabundance of acid on the base, the excess of acid is not simply mixed with the neutral salt, but is chemically combined and that in *une juste quantité*, otherwise expressed in a fixed and definite proportion. The affinity of the alkali for the acid is not completely exhausted, so to speak, by the formation of the acid salt.

H. Rose [2] found that powdered potassium sulphate slowly absorbs the vapour of sulphuric acid. Mixed soln. of the alkali sulphates and sulphuric acid deposit double salts whose *composition is determined by the temp., the conc., and the* relative proportions of acid and salt in soln. For example, a conc. soln. containing equi-molecular proportions of potassium sulphate and potassium hydrosulphate will give monoclinic plates of the salt $K_3H(SO_4)_2$, that is, $K_2SO_4.KHSO_4$. The proportion of normal sulphate in a mixed soln. of potassium sulphate and sulphuric acid increases proportionally with decreasing amounts of acid, until, when the proportion is $K_2SO_4 : H_2SO_4 = 2 : 1$, the solid phase is entirely normal sulphate. Dil. soln. containing $K_2SO_4 : H_2SO_4 = 1 : 2$ to 3, give monoclinic plates of $K_2SO_4.3KHSO_4.H_2O$; while conc. soln. give needle-like crystals of the salt $K_2SO_4.6KHSO_4$, which is rather unstable and readily breaks down into $K_2SO_4.3KHSO_4$ and $KHSO_4$. Similarly with soln. of sodium sulphate and sulphuric acid. If the number of mols. of normal sulphate, Na_2SO_4, and of sulphuric acid, H_2SO_4, in equilibrium with a solid phase or phases at 25°, be plotted, a curve will be obtained with breaks as illustrated in Fig. 43,

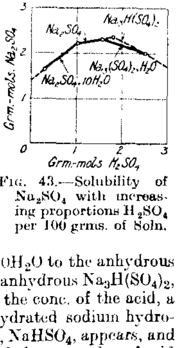


FIG. 43.—Solubility of Na_2SO_4 with increasing proportions H_2SO_4 per 100 grms. of Soln.

which shows the limiting conc. for the passage from $Na_2SO_4.10H_2O$ to the anhydrous sulphate, Na_2SO_4, thence to the trisodium hydrodisulphate, anhydrous $Na_3H(SO_4)_2$, or hydrated $Na_2H(SO_4)_2.H_2O$. With a greater increase in the conc. of the acid, a break appears corresponding with the formation of monohydrated sodium hydrosulphate, $NaHSO_4.H_2O$; then the anhydrous hydrosulphate, $NaHSO_4$, appears, and the curve joins on to that depicted in Fig. 47. A comparatively large number of acid sulphates of potassium, $xH_2SO_4.yK_2SO_4$, have been reported which are not paralleled by companions of the other alkalies, not necessarily because such compounds do not exist, but because they have not been sought. Some of the alleged compounds may be mixtures, because the evidence of unique chemical individuality is not always forthcoming. The phase-rule test applied by W. Stortenbeker, C. G. A. van Dorp and J. d'Ans [3] has shown the existence of the following potassium, sodium, and lithium compounds with definite conditions of stability between 18° and −25°. To these have been added the well-defined anhydro- or pyro-sulphates, $M_2S_2O_7$, and the reported parallel compounds of the other alkalies.

Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
—	$Na_3H(SO_4)_2$	$K_3H(SO_4)_2$	—	—
$Li_2H_4(SO_4)_3$	$Na_2H_4(SO_4)_3$	—	—	—
—	—	$K_5H_3(SO_4)_4$	—	—
—	—	$K_8H_6(SO_4)_7$	—	—

Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
$LiHSO_4$	$NaHSO_4$	$KHSO_4$	$RbHSO_4$	$CsHSO_4$
—	$NaHSO_4.H_2O$	—	—	—
—	$NaH_3(SO_4)_2$	$KH_3(SO_4)_2$	—	—
—	$NaH_3(SO_4)_2.H_2O$	$KH_3(SO_4)_2.H_2O$	—	—
$Li_2SO_4.7H_2SO_4$	—	—	—	—
—	$2Na_2SO_4.9H_2SO_4$	—	—	—
—	$Na_2S_2O_7$	$K_2S_2O_7$	$Rb_2S_2O_7$	$Cs_2S_2O_7$
—	$NaHS_2O_7$	KHS_2O_7	—	—

The general results are in agreement with the rule that the stability of an additive compound increases with the differences in character—positive or negative—of its components.

G. C. A. van Dorp's curves for the ternary system: lithium sulphate, sulphuric acid and water, are shown in Fig. 44. The solid phases *AB* represent the monohydrated sulphate, $Li_2SO_4.H_2O$; *BC*, the anhydrous sulphate, Li_2SO_4; and *CD*, the hydrosulphate, $LiHSO_4$. J. Kendall and M. L. Landon found on the f.p. curve of the binary mixture evidence of the hydrosulphate unstable at its m.p. 170·5°; of **dilithium tetrahydrotrisulphate,** $Li_2SO_4.2H_2SO_4$, unstable at its m.p. and passing into the hydrosulphate at 50°; and of **lithium heptahydrotetrasulphate,** $Li_2SO_4.7H_2SO_4$, or $LiH_7(SO_4)_4$, with a m.p. 13·6°.

P. Pascal and M. Ero also studied the ternary system, $Na_2SO_4-H_2SO_4-H_2O$.

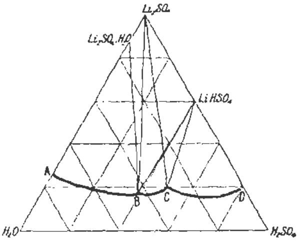


FIG. 44.—Ternary System, $Li_2SO_4-H_2SO_4-H_2O$, at 30°.

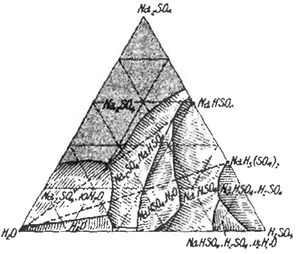


FIG. 45.—Regions of Stability of the Solid Phases in the Ternary System, $H_2SO_4-Na_2SO_4-H_2O$ (P. Pascal and M. Ero).

and found the solid phases and their domains of stability which are indicated in Fig. 45. The compound **trisodium hydrodisulphate,** $Na_3H(SO_4)_2$, *i.e.* $(Na_2SO_4)_3H_2SO_4$, or $Na_2SO_4.NaHSO_4$, was obtained by T. Thomson,[4] in 1825, during the evaporation of the product left after heating sulphuric acid with sodium chloride in the preparation of hydrogen chloride. H. Rose, G. F. Brindley, C. W. Volney, C. Schulz, and K. Heumann seem to have made **monohydrated trisodium hydrodisulphate,** $Na_3H(SO_4)_2.H_2O$, and although G. C. Wittstein denied the existence of this salt J. C. G. de Marignac (1857) obtained needle-like crystals of $Na_3H(SO_4)_2$, and showed that they belong to the monoclinic system with the axial ratios: $a:b:c=1·7216:1:0·9485$; $\beta=102°\ 16'$. C. W. Volney also obtained these same crystals by heating a mixture of sodium nitrate and sulphuric acid to a temp. not exceeding 100°, and allowing the oily liquid, decanted from the undecomposed nitrate, to crystallize. J. d'Ans obtained the crystals by evaporating soln. containing a mixture of equi-molecular proportions of sodium sulphate and sulphuric acid at about 100° until crystals began to appear. Larger crystals of the desired salt are obtained by slowly cooling the soln. The crystals are first washed with a mixture of 50 c.c. of water, 10 c.c. of conc. sulphuric acid, and 75 c.c. of alcohol, and finally with alcohol alone, and then with ether. Crystals of the monohydrated

salt are difficult to obtain. J. d'Ans obtained a crop by mixing the limiting soln., $Na_2SO_4—Na_2HSO_4$, Fig. 45, with glauberite, $CaNa_2(SO_4)_2$, and keeping the mixture at 25° for about a week. Further crops of the monohydrated salt were obtained by using these crystals for seeding the original soln. According to H. Lescœur, P. Pascal and M. Ero, the hydrated form is $NaHSO_4.H_2SO_4.1\frac{1}{2}H_2O$. H. Rose [5] prepared the corresponding **tripotassium hydro-disulphate**, $K_3H(SO_4)_2$, or $(K_2SO_4)_3H_2SO_4$; or $K_2SO_4.KHSO_4$, as a product in the action of sulphuric acid on nitre. These crystals also appear in the first crop which separates during the evaporation of an aq. soln. of the hydrosulphate, $KHSO_4$. W. Stortenbeker found them as the solid phase when the liquid contained $H_2SO_4 : K_2SO_4=1·15$ to 1·80. A. Scacchi stated the crystals belonged to the rhombic system, but J. C. G. de Marignac's measurements of the angles, and G. Wyrouboff's determination of the optical properties of the crystals, showed that they belong to the monoclinic system with axial ratios $a:b:c=1·769:1:2·628$; $\beta=102°$ 41′. Their sp. gr. is 2·599 (B. Gossner), or 2·587 (W. Stortenbeker). J. Kendall and M. L. Landon observed indications of this compound on the f.p. curve of binary mixtures of the salt and acid; its m.p. is 91·5°.

The salt **pentapotassium trihydrotetrasulphate**, $K_5H_3(SO_4)_4$, that is, $5K_2SO_4.3H_2SO_4$, or $K_2SO_4.3KHSO_4$, was reported by W. Stortenbeker [6] to have a narrow range of stability on the equilibrium diagram at 18°, with soln. of a mol. of a neutral salt and 2·07 mols. of sulphuric acid. The monoclinic crystals of the monohydrated salt, $K_2SO_4.3KHSO_4.H_2O$, have the axial ratios $a:b:c=1·708:1:2·748$; $\beta=113°$ 59′. J. d'Ans could not find this salt at 25°, although he obtained evidence of its existence at 18°, and at 0°. Its sp. gr. is given by W. Stortenbeker [7] at 2·463 (18°). A salt, $K_4H_2(SO_4)_3$, that is, $2K_2SO_4.H_2SO_4$, or $K_2SO_4.2KHSO_4$, was reported by R. Phillips,[8] in 1821, to separate in needle-like crystals from soln. of the normal salt in dil. sulphuric acid. It has not been located on the equilibrium diagram, but W. Stortenbeker considers Phillips' salt to be **octopotassium hexahydroheptasulphate**, $K_8H_6(SO_4)_7$, that is, $4K_2SO_4.3H_2SO_4$, or $K_2SO_4.6KHSO_4$. Crystals of this salt were recognized by A. Scacchi [9] among certain volcanic products, and this salt is one of the leading constituents of the mineral *misénite* found in the Grotto del Solfo at Miseno (near Naples). According to W. Stortenbeker, it is formed in soln. with $H_2SO_4 : K_2SO_4=2·18:1$. It has a very narrow range of stability, and J. d'Ans recognized it at 0° and 18°, but not at 25°. W. Stortenbeker gives its sp. gr. as 2·327 (18°), A. Jacquelain, 2·277 (18°), and G. Wyrouboff, 2·245. The curve *AB* in the portion of the triangular diagram, Fig. 46, refers to the phase K_2SO_4; *BC*, the phase $K_3H(SO_4)_3$; *CD*, the phase, $K_2SO_4.6H_2SO_4$; and *DE*, to the phase $KHSO_4$. A minute portion at *C*, applied to the phase $K_2SO_4.3KHSO_4$. C. Schultz [10] obtained thin plates of **dilithium tetrahydrotrisulphate**; $Li_2H_4(SO_4)_3$, *i.e.* $2LiHSO_4.H_2SO_4$, or $Li_2SO_4.2H_2SO_4$, melting at 110°, from a soln. of lithium sulphate in not quite four parts of its weight of conc. sulphuric acid G. C. A. van Dorp did not find this salt at 30°; but J. Kendall and M. L. Landon, on the f.p. curve, found evidence of it existing as unstable at the m.p. and passing into $LiHSO_4$ at 50°; they also found **disodium tetrahydrotrisulphate**, $Na_2H_4(SO_4)_3$, existing in two modifications both unstable at the m.p., and passing into $NaHSO_4$ at 95° and 109°.

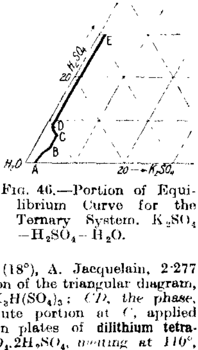


FIG. 46.—Portion of Equilibrium Curve for the Ternary System. $K_2SO_4—H_2SO_4—H_2O$.

A. Arfvedson [11] noticed, in 1818, that the sulphate prepared by the evaporation of a soln. of lithium sulphate in sulphuric acid melts more readily than the normal sulphate crystallized from neutral soln.; and C. G. Gmelin found that A. Arfvedson's salt contained a greater proportion of sulphuric acid than the normal salt, for the latter was obtained by expelling water, sulphur dioxide, and oxygen from the former by calcination. In 1868, C. Schultz prepared crystals of **lithium hydrosulphate**, $LiHSO_4$, separated from a soln. of the normal sulphate in sulphuric acid of sp. gr. 1·6 to 1·7. Very fine crystals of this salt can be obtained by recrystallization from its aq. soln. According to H. Lescœur, this compound is formed only when monohydrated sulphuric acid is mixed with the normal sulphate. According

to J. Kendall and M. L. Landon, it appears on the f.p. curve of the components, and it has an unstable m.p. of 170·5°.

The corresponding **sodium hydrosulphate,** $NaHSO_4$, was obtained by J. J. Berzelius by heating to about 550°, a mixture of ten parts of sodium sulphate with seven of conc. sulphuric acid until all was in quiet fusion. If the temp. is too high, sodium pyrosulphate, $Na_2S_2O_7$, is formed. Triclinic four-sided prisms are obtained by recrystallization from hot water, and T. Thomson obtained the same salt by the evaporation of a soln. of Glauber's salt in dil. sulphuric acid. According to J. C. G. de Marignac, if the temp. of crystallization is below 50°, crystals of a hydrated form of sodium hydrosulphate were once thought to be formed, but T. Graham (1835) says that he never succeeded in finding any water of crystallization, and that the reports of its occasional presence are founded on dubious evidence, being possibly based on analyses of mixtures of the hydrosulphate with a little Glauber's salt. The reason why sodium potassium hydrosulphate should be crystallized from soln. at a high temp., says T. Graham, is because the soln. at low temp. are apt to decompose into the normal sulphate and sulphuric acid. This decomposition may occur even when the soln. contains an excess of sulphuric acid, and this the more readily with sodium than with potassium hydrosulphate, and R. Brandes and E. Firnhaber say that crystals of Glauber's salt alone separate on cooling a hot soln. of one part of sodium hydrosulphate in four parts of water.

If 20 grms. of sulphuric acid be diluted with 100 c.c. of water, and the liquid divided into two equal parts, one part neutralized with a soln. of sodium hydroxide and then mixed with the other, crystals of sodium monohydrated sulphate will be obtained if the filtered soln. be conc. by evaporation, and allowed to crystallize from a cold soln. in a desiccator.

J. Kendall and M. L. Landon obtained evidence of sodium hydrosulphate on the f.p. curve of the components, and gave the m.p. as 186°. J. C. G. de Marignac (1857), however, claimed to have obtained monoclinic prisms of **hydrated sodium hydrosulphate,** $NaHSO_4.H_2O$, with axial ratios: $a:b:c=0·9965:1:1·0480$; $\beta=119° 35'$, by cooling a soln. of sodium sulphate with an excess of sulphuric acid, and he said that it is probably this salt which J. J. Berzelius and T. Thomson believed to contain three mols. of water of crystallization, and which R. Brandes' analyses represent as containing 22·3° per cent. of Na_2O; 57·24 per cent. of SO_3; and 20·46 per cent. of H_2O—*i.e.* $Na_2SO_4.H_2SO_4.2H_2O$, or $NaHSO_4.H_2O$; T. Graham's analysis: Na_2O, 25·96 per cent., SO_3, 66·55; and H_2O, 7·49 per cent. corresponds with $NaHSO_4$. J. C. G. de Marignac's analysis agreed with that of R. Brandes. H. Rose also claims to have made the monohydrated salt by the action of a mixture of sodium chloride with twice its weight of sulphuric acid mixed with one-tenth its weight of water; and J. d'Ans and P. Pascal and M. Ero have shown the limits of stability of the monohydrated salt in soln. of dil. sulphuric acid and sodium sulphate.

J. d'Ans [12] has investigated the equilibrium conditions at 25°, of the ternary system: $Na_2O-SO_3-H_2O$. He recognizes the existence of

Sodium hydrosulphate	$NaHSO_4$
Hydrated sodium trihydrodisulphate	$NaH_3(SO_4)_2.H_2O$
Disodium sulphate hemienneasulphuric acid	$Na_2SO_4.4·5H_2SO_4$
Sodium hydro-pyrosulphate, or sodium hydrogen anhydro-sulphate	$NaHS_2O_7$
Sodium pyrosulphate, or sodium anhydro-sulphate	$Na_2S_2O_7$

The isothermal solubility curve of mixtures of sodium sulphate, Na_2SO_4, with soln. of sulphur trioxide in water, at 25°, is shown in Fig. 47. The numbers are expressed in mols. of Na_2SO_4 or SO_3 in 1000 grms. of soln. The ternary system, $Na_2O-SO_3-H_2O$, diagrammed in Fig. 48, is extended towards the SO_3 apex as far as the formation of $NaHS_2O_7$, but not so far as the well-known sodium pyrosulphate, $Na_2S_2O_7$. The composition of the solid phases corresponds with the existence of sodium hydrosulphate, $NaHSO_4$; and monohydrated sodium trihydro-disulphate,

$NaH_3.(SO_4)_2.H_2O$; and sodium dihydrogen anhydro-sulphate, $NaHS_2O_7$, that is, $NaHSO_4.SO_3$. There is also $Na_2SO_4.4{\cdot}5H_2SO_4$, or $2Na_2SO_4.9H_2SO_4$. In Fig. 48, the triangle is cut into two portions by the heavier line—the smaller portion represents a complex of the three components which forms an unsaturated soln.; and the larger portion, a complex which splits into a soln. and one or two solid phases. The light lines have been drawn to show how the separation occurs. As explained in connection with the triangular diagrams for sodium and potassium iodates: any point in the sectors represents a soln. which splits into a soln. whose composition is represented by a point on the heavier curve bounding the sector, and into the solid phase named in connection with that sector: points outside these sectors represent soln. which separate into soln. and two solid phases. The heavier curves in Figs. 47 and 48 represent the composition of a soln. which remains constant while the composition of the solid phase (or phases) changes.

The composition of the soln. in equilibrium, with one or two solid phases, is represented by the heavier curves in the diagram; starting from hydrated sodium hydroxide, $NaOH.H_2O$, and representing the percentage proportions of the three components in the order $Na_2O : SO_3 : H_2O$, the soln. contains 16·84 : 0 : 83·16 : the curve leading from this point represents a soln. in equilibrium with the solid phases: $NaOH.Na_2O$ and $Na_2SO_4.10H_2O$: at the *first maximum* (3·31 : 3·31 : 93·38) the solid phase is decahydrated sodium sulphate,

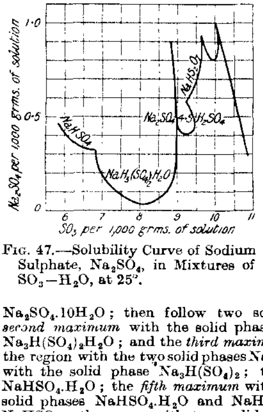


FIG. 47.—Solubility Curve of Sodium Sulphate, Na_2SO_4, in Mixtures of SO_3-H_2O, at 25°.

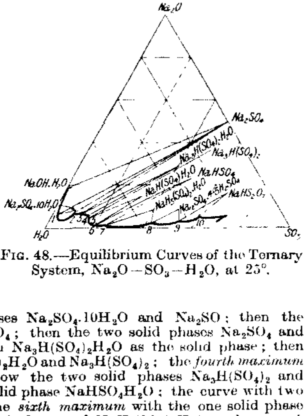


FIG. 48.—Equilibrium Curves of the Ternary System, $Na_2O-SO_3-H_2O$, at 25°.

$Na_2SO_4.10H_2O$; then follow two solid phases $Na_2SO_4.10H_2O$ and Na_2SO; then the *second maximum* with the solid phase Na_2SO_4; then the two solid phases Na_2SO_4 and $Na_3H(SO_4)_2H_2O$; and the *third maximum* with $Na_3H(SO_4)_2H_2O$ as the solid phase; then the region with the two solid phases $Na_3H(SO_4)_2H_2O$ and $Na_3H(SO_4)_2$; the *fourth maximum* with the solid phase $Na_3H(SO_4)_2$; then follow the two solid phases $Na_3H(SO_4)_2$ and $NaHSO_4.H_2O$; the *fifth maximum* with the solid phase $NaHSO_4H_2O$; the curve with two solid phases $NaHSO_4.H_2O$ and $NaHSO_4$; the *sixth maximum* with the one solid phase $NaHSO_4$; the curve with two solid phases $NaHSO_4$ and $NaH_3(SO_4)_2H_2O$; the *seventh maximum* (0·13 : 29·86 : 70·02) with the solid phase $NaH_3(SO_4)_2H_2O$; the curve with two solid phases $NaH_3(SO_4)_2H_2O$ and $Na_2SO_4.4{\cdot}5H_2SO_4$ or the metastable $NaH_3(SO_4)_2H_2O$; the *eighth maximum* (1·80 : 43·20 : 55·00) with the solid phase $Na_2SO_4.4{\cdot}5H_2SO_4$; the curve with the two solid phases $Na_2SO_4.4{\cdot}5H_2SO_4$; the curve with the two solid phases $Na_2SO_4.4{\cdot}5H_2SO_4$ and $NaHS_2O_7$; the *ninth maximum**(5·58 : 60·44 : 34·03) with the solid phase $NaHS_2O_7$; and so on into the region still unexplored.

According to J. d'Ans, the range of stability of monohydrated sodium hydrosulphate, $NaHSO_4.H_2O$, at 25°, is approximately with soln. containing from 1·95 mols. of Na_2SO_4, 3·12 mols. of H_2SO_4 per 1000 grms. of soln., to $0{\cdot}47Na_2SO_4+4{\cdot}96H_2SO_4$ per 1000 grms.; and of the anhydrous salt, $NaHSO_4$, with from the latter conc. up to 0·305 mol. of Na_2SO_4 and 6·87 mols. of sulphuric acid per 1000 grms. of soln. With rather higher conc. of sulphuric acid, the trihydrodisulphate, $NaH_3(SO_4)_2$, appears. These ranges of conc. give the turning-points curve, Fig. 47, carried

towards the left. The hydrated salt, $NaHSO_4H_2O$, melts at 58·54° ± 0·05°, and J. d'Ans suggests its use as a fixed point for thermometry. The monohydrated salt does not appear in the isothermal curve above the transition temp. 58·54°.

The corresponding **potassium hydrosulphate,** $KHSO_4$, is obtained by melting together equi-molecular parts of potassium sulphate and sulphuric acid. According to V. A. Jacquelain,[13] a hot soln. of a mol. of potassium sulphate with a mixture of 0·5 to 1·0 mol. of sulphuric acid and water yields crystals of the normal salt on cooling, and the mother liquid when evaporated furnishes needle-like crystals of potassium pyrosulphate; the last-named salt is also obtained as a crystalline mass by concentrating a soln. of a mol. of the normal sulphate in 1·5 to 2·0 mols. of sulphuric acid, but after the crystalline mass has been exposed five days, it yields rhombohedral crystals of potassium hydrosulphate; the change occurs more quickly if three mols. are used; and in an hour, if five mols. of acid are used per mol. of potassium sulphate. The hydrosulphate, $KHSO_4$, and the pyrosulphate, $K_2S_2O_7$, can be formed as readily at ordinary temp. as at 40°, the latter is the more readily produced when the sulphuric acid is in excess, the former when only a small quantity of the acid is present. V. A. Jacquelain further showed that the rhombohedral crystals of the hydrosulphate are readily produced from a soln. of equimolecular parts of potassium sulphate and sulphuric acid in a hot dil. soln. of hydrochloric, nitric, tartaric, or acetic acid—hence, these acids act in the same manner as an excess of sulphuric acid.

When the residue left after the distillation of nitric acid from a mixture of a mol. of potassium nitrate with two mols. of sulphuric acid is dissolved in hot water, the first crop of crystals, says P. Geiger, is potassium sulphate, and the mother liquid on standing in a cool place first deposits needle-like crystals of the anhydro-sulphate, and then thick prismatic crystals of the hydrosulphate. According to C. W. Volney, if the temp. in the retort has not exceeded 100°, and sodium nitrate is used, the oily mass decanted from the undecomposed nitrate, deposits crystals of $NaH_3(SO_4)_2$; if the temp. has not exceeded 121°, the crystals are sodium hydrosulphate, $NaHSO_4$. H. Rose claims to have made the monohydrated salt, $KHSO_4.H_2O$, and J. B. Senderens the 5½-hydrated salt, $KHSO_4.5\frac{1}{2}H_2O$, but in neither case is there any satisfactory evidence of the chemical individuality of the alleged hydrates.

G. Tschermak also obtained crystals of potassium hydrosulphate, $KHSO_4$, by the slow decomposition of potassium ethyl sulphate, or by treating alcoholic potash with sulphuric acid. J. Kendall and M. L. Landon obtained evidence of the hydrosulphate from the f.p. curve of the components; its m.p. is given as 218·6°, and there are three modifications with transition points at 182° and 202°.

It is therefore evident that the composition of the salt deposited by a soln. of potassium sulphate in sulphuric acid is determined (i) by the ratio of free acid to salt, (ii) by the conc. of the soln., and (iii) on the temp. According to W. Stortenbeker,[14] the hydrosulphate, $KHSO_4$, crystallizes from soln. of potassium sulphate and sulphuric acid in which the ratio $H_2SO_4 : K_2SO_4$ is greater than 4·5; and he has studied the ranges of stability of the different compounds of potassium sulphate, sulphuric acid, and water. J. d'Ans recognizes the existence of the compounds:

Potassium hydrosulphate	$KHSO_4$
Hydrated potassium trihydrodisulphate	$KH_3(SO_4)_2.H_2O$
Potassium trihydrodisulphate	$KH_3(SO_4)_2$
Potassium hydro-pyrosulphate	KHS_2O_7
Potassium pyrosulphate	$K_2S_2O_7$

The isothermal solubility curve of mixtures of potassium sulphate and sulphuric acid expresses the composition of the soln. at 25° in equilibrium with the solid phase or phases, when the mol. ratio of K_2SO_4 and SO_3 per 1000 grms. of soln. are plotted as co-ordinates. The ranges of stability in the ternary system: $K_2O-SO_3-H_2O$, are diagrammed in Fig. 51, where the conditions have been studied in the vicinity of the SO_3-apex, as far as the formation of KHS_2O_7, but not as far as the well-known potassium pyrosulphate. The meaning of the diagram

will be evident after the description of the corresponding diagram for the ternary system: $Na_2O-SO_3-H_2O$, Fig. 48. The maximal points represent the composition of the soln. in equilibrium with solid phases: (1) K_2SO_4; (2) $K_3H(SO_4)_2$; (3) $K_2SO_4.6KHSO_4.H_2O$; (4) $KHSO_4$; (5) $KH_3(SO_4)_2.H_2O$; (6) KHS_2O_7.

R. Bunsen, H. Erdmann, and others[15] have made rubidium hydrosulphate, $RbHSO_4$. It is obtained by heating the rubidium salt of a volatile acid with sulphuric acid to about 250°–257°; the oily liquid, on cooling, forms a crystalline mass of this salt. R. Bunsen made cæsium hydrosulphate, $CsHSO_4$, by treating cæsium carbonate with sulphuric acid under similar conditions. Both salts crystallize from water in rhombic crystals.

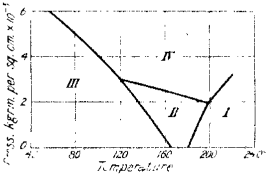


FIG. 49.—Pressure-Temperature Equilibrium Diagram of Potassium Hydrosulphate.

The **crystals** of sodium hydrosulphate, $NaHSO_4$, form triclinic crystals which, according to J. C. G. de Marignac, have the axial ratios: $a:b:c=0.7740:1:1.1981$; $\alpha=94°\ 54'$; $\beta=93°\ 13'$; $\lambda=88°\ 57'$. The crystals of potassium hydrosulphate are rhombic bipyramids with axial ratios: $a:b:c=0.8609:1:1.9344$, and with a positive double refraction. P. W. Bridgman[16] found that there are four modifications of potassium hydrosulphate. P. Groth has pointed out that potassium hydrosulphate forms three series of mixed crystals with ammonium hydrosulphate, and therefore inferred that the salt might prove to be trimorphic. It has not yet been shown if any of the forms stable at high temp. and atm. press. belong to the crystal systems corresponding with the mixed crystals under consideration, although P. W. Bridgman says that the dissimilarity in the phase diagrams of the two salts, shows that the isopolymorphism is more complex than is indicated by the mixed crystal systems at atm. temp. The equilibrium diagram is shown in Fig. 49. A few selected measurements are indicated in

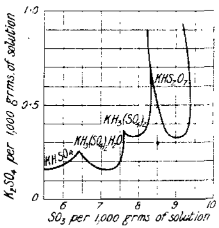


FIG. 50.—Solubility Curve of Potassium Sulphate, K_2SO_4, in Mixtures of SO_3+H_2O, at 25°.

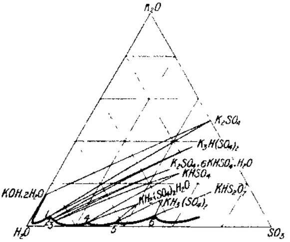


FIG. 51.—Equilibrium Curve of the Ternary System, $K_2O-SO_3-H_2O$, at 25°.

Table XXXIX. At the triple points I–II–IV, 1830 kgrms. per sq. cm. press., and 198·6°, the changes of vol. for I–II, II–IV, and I–IV are respectively 0·00197, 0·00113, and 0·00310 c.c. per grm., and the latent heats respectively 0·939, 0·711, and 0·865 kgrm. m. per grm. At the triple point II–III–IV, 2900 kgrms. per sq. cm. and 118·2°, the changes in vol. for the transitions II–III, II–IV, and III–IV, are respectively 0·00570, 0·00110, and 0·00680 c.c. per grm., and the latent heats respectively 1·41, 0·057, and 1·47 kgrm. m. per grm.

W. Spring[17] gives the **specific gravity** of lithium hydrosulphate as 2·123 (13°);

of the sodium salt, 2·435 (13°); and of the potassium salt, 2·302 (13°); A. Jacquelain also gives 2·163 for the potassium salt; L. Playfair and J. P. Joule, 2·478;

TABLE XXXIX.—EFFECT OF PRESSURE ON THE TRANSITION TEMPERATURE OF POTASSIUM HYDROSULPHATE.

Press.		Transition temp.	Change of vol. c.c. per grm.	Latent heat kgrm.-m. per grm.
I–II	1	180·5°	0·00066	0·302
	2000	200·3°	0·00209	1·000
I–IV	2000	201·5°	0·00307	0·801
	3000	218·4°	0·00290	0·756
II–IV	1810	200·0°	0·00113	0·071
	2875	120·0°	0·00110	0·059
II–III	1	164·2°	0·00556	1·54
	3000	116·6°	0·00571	1·41
III–IV	3000	116·4°	0·0068	1·46
	6000	51·4°	0·0058	0·70

B. Gossner, 2·322; G. Wyrouboff, 2·273; H. G. F. Schröder, 2·305; and W. Stortenbeker, 2·314. According to W. Spring, the sp. gr. of rubidium hydrosulphate is 2·892 (16°), and of the cæsium salt, 3·352 (16°). The mol. vol. are:

	$2LiHSO_4$	$2NaHSO_4$	$2KHSO_4$	$2RbHSO_4$	$2CsHSO_4$
Sp. gr.	2·123	2·435	2·302	2·892	3·352
Mol. vol.	98·1	98·6	118·0	125·8	136·6

These numbers are less than the joint mol. vol. of the components—neutral sulphate and sulphuric acid, *e.g.* for sulphuric acid, H_2SO_4, the mol. vol. is 53·2, and for sodium sulphate 53·2, and hence for $2NaHSO_4$, the calculated mol. vol. is $53·2+53·2=106·4$, the observed value is 98·6. The decomposition of the hydrosulphate into these two components must therefore occur with an increase in volume. Similar remarks apply to lithium hydrosulphate. W. Spring was hence led to try the effect of a very high press. at a low temp.—under 30°. He found, in accord with H. le Chatelier's principle, that the raising of the press. favoured the reaction which formed the products with the smaller volume. With acid sulphates containing a high content of water, W. Spring found a separation into an acid liquid, and a less acid solid.

T. Thomson[18] observed no loss in weight when sodium hydrosulphate is heated to 149°. According to T. Graham, this salt does not lose its transparency at this temp., its **melting point** is over 315°, and, when heated to a still higher temp., it loses sulphuric acid—according to K. Kraut, a part decomposes into sulphuric acid and normal sulphate, and a part into water and pyrosulphate, $Na_2S_2O_7$. T. Graham also found potassium hydrosulphate to retain its transparency at 149°, and to melt at 315·5° to a clear oily liquid without appreciable decomposition. J. L. Gay Lussac observed no decomposition of this salt below a red heat, but at a red heat, it decomposes into sulphuric acid, sulphur dioxide, and oxygen as in the case of the sodium salt. A. Jacquelain gives 190° as the m.p. of the potassium salt; E. Mitscherlich, 200°; C. Schultz, 210°. R. Bunsen says that rubidium hydrosulphate melts below a red heat, and as a red heat is approached it begins to foam, loses sulphuric acid, and finally forms the normal sulphate; but, says P. E. Browning, the pyrosulphate, $Rb_2S_2O_7$, is first formed, and this decomposes into the normal salt with great difficulty. R. Bunsen applied similar remarks to cæsium hydrosulphate.

Solid potassium hydrosulphate, says H. Kopp,[19] has a sp. ht. 0·244 between 19° and 51°. According to M. Berthelot, the **heat of neutralization,** $NaOH+H_2SO_4=-14·7$ Cals. when all is in soln., if solid, 16·00 Cals., and therefore the **heat of**

solution is 1·87 Cals. J. Thomsen gives +1·19 Cal. The heat of neutralization, $KOH+H_2SO_4$=14·6 Cals. when all is in soln., and 48·2 Cals. when all is solid. For $2KOH+H_2SO_4$, all in soln., 31·7 Cals., *i.e.* 2×15·85 Cals., consequently, $KHSO_4+KOH$, all in soln., 17·1 Cals., and $K_2SO_4+H_2SO_4$, all in soln., −2·5 Cals., so that the formation of normal potassium sulphate from the bisulphate and potassium hydroxide evolves 17·1 Cals., while the neutralization of $\frac{1}{2}H_2SO_4$ by KOH evolves 15·85 Cals. A. Colson [20] explains the variation in the negative heat of soln. of potassium hydrosulphate which becomes less as the dilution increases by the more and more complete dissociation of the acid salt, and the formation of the normal salt. The normal salt can exist in presence of the free acid; and the dissociation of the hydrosulphate is decreased by increasing the conc. of the acid, or by increasing the conc. of the normal sulphate; and it is increased by increasing dilution. The reaction, H_2SO_4+K, all solid, evolves 79·2 Cals., and H_2SO_4+2K, all solid, 144·80 Cals. Hence, the displacement of one hydrogen atom from sulphuric acid by potassium disengages 79·2 Cals., and the second hydrogen atom, 65·5 Cals. The **heat of formation** of sodium hydrosulphate: $Na+H+O_2+SO_2$ is 196·31 Cals. (M. Berthelot), and of potassium hydrosulphate, 206·02 Cals. $K_{solu.}+H_{gas}+H_{soln.}+4O_{gas}$=273·24 Cals. According to R. de Forcrand, the heat of formation of rubidium hydrosulphate from its elements is 277·34 Cals., and of cæsium hydrosulphate, 282·9 Cals. According to J. Thomsen, the **heat of dilution,** $(NaHSO_4+10H_2O)+800H_2O$, is 1·0 Cal.: $Na_2SO_4+2H_2SO_4$=2·35 Cals.; and $Na_2SO_4+4H_2SO_4$=2·68 Cals. For $KHSO_4+330H_2O$, at 15°, M. Berthelot gives −3·23 Cals., but the value of the constant varies with the proportion of water; thus, for $20H_2O$, −3·91 Cals.; $5H_2O$, −3·97 Cals.; $100H_2O$, −3·94; for $200H_2O$, −3·80 Cals.; for $400H_2O$, −3·53 Cals.; and for $800H_2O$, −3·14 Cals. For the heat of admixture, $K_2SO_4+H_2SO_4$, J. Thomsen gives 16·64 Cals., and M. Berthelot 15·2 Cals. P. Chroustschoff found that the heat of reaction for mixtures of potassium sulphate and sulphuric acid attains a maximum when these two compounds are in the proportion $10K_2SO_4:H_2SO_4$. R. de Forcrand found the heat of soln. of rubidium hydrosulphate, $RbHSO_4$, to be −3·73 Cals., and of cæsium hydrosulphate, −3·73 Cals.

The **solubility** of sodium hydrosulphate in water is represented by 28·6 grms. at 25° and 50 grms. at 100°, per 100 grms. of water; and P. Kremers [21] gave the solubility of potassium hydrosulphate in 100 grms. of water at 0°, as 36·3 grms.; at 20°, 51·4 grms.; at 40°, 67·3 grms.; and at 100°, 121·6 grms. 100 grms. of alcohol at 25° dissolve 1·4 grms. of sodium hydrosulphate. A soln. of potassium hydrosulphate in about half its weight of boiling water deposits needle-like crystals on cooling; according to P. L. Geiger,[22] a large proportion of the crystals consist of the normal salt, and some sulphuric acid remains in soln., and this the more, the larger the proportion of water to salt. If the proportion of water is great, the addition of a large amount of sulphuric acid to the water will not prevent the separation of normal sulphate. According to T. Graham, the affinity of the water for sulphuric acid overcomes that of the salt for the same acid; and H. Rose, after noting the transformation of the hydrosulphate by repeated crystallization into intermediate sulphates, and finally into normal sulphate, attributed the transformation to the action of water which, in virtue of its preponderating mass, united with the sulphuric acid associated with the normal sulphate in the hydrosulphate. Cold water extracts far more sulphuric acid from the solid salt, leaving much normal sulphate behind; the transparent crystals become translucent under these conditions. The decomposition of sodium hydrosulphate by water is greater than with the potassium salt. Boiling alcohol removes almost nothing but sulphuric acid from powdered potassium or sodium hydrosulphates. The conditions of equilibrium for the alkali sulphates in the presence of different proportions of acid have been partially elucidated by J. d'Ans [23] in his work: *Zur Kenntnis der sauren Sulfate;* and by W. Stortenbeker in his work: *Sur les sulfates de potassium.*

J. C. G. de Marignac's values for the **specific gravities** of soln. of sodium hydrosulphate,[24] at 20°, are:

Per cent. $NaHSO_4$	3·23	6·26	11·50	21·05
Sp. gr.	1·0236	1·0472	1·0917	1·1705

and for soln. of potassium hydrosulphate, at 18°, F. Kohlrausch found:

Per cent. $KHSO_4$	5	10	15	20	25	27
Sp. gr.	1·0354	1·0726	1·1116	1·1516	1·1920	1·2110

The **viscosities** of soln. of sodium hydrosulphate determined by E. B. Moore,[25] at 18°, are 1·059 (water unity) for 0·25 mol. per litre, 1·100, 1·260, 1·622, and 1·874, for 0·5, 1, 2, and 4 mols. per litre respectively.

The **coefficients of cubical expansion** of soln. of potassium hydrosulphate, determined by C. Forch,[26] are for soln. with 34 grms. of $KHSO_4$ per litre, 0·000086 (0°–5°); 0·000149 (5°–10°); 0·000411 (34°–40°); for soln. with 68 grms. of $KHSO_4$ per litre, 0·000173 (0°–5°); 0·000222 (5°–10°); and 0·000441 (35°–40°): and for soln. with 136 grms. of $KHSO_4$ per litre, 0·000305 (0°–5°); 0·000335 (5°–10°); and 0·000492 (35°–40°).

P. Kremers [27] places the **boiling point** of a sat. aq. soln. of potassium hydrosulphate at 103°; and F. M. Raoult found that a gram of the salt in 100 grms. of water lowers the f.p. 0·384°, or 34·8°, per mol. G. Tammann measured the lowering of the **vapour pressure** of water at 100° for soln. of potassium hydrosulphate containing from 11·16 to 115·66 grms. per 100 grms. of water, and for the terminal soln. of the series found a lowering of 18 mm. and 179·6 mm. of mercury respectively.

K. Barth's [28] values for the **electrical conductivity** λ of soln. of sodium and potassium hydrosulphates at 25° and containing a mol. of salt in v litres of water:

v	32	64	128	256	512	1024
λ, $NaHSO_4$	311·9	366·2	408·3	449·9	488·0	513·0
λ, $KHSO_4$	339·5	384·5	428·3	469·9	507·4	530·8

The relatively large values of the conductivities, and the relatively fast increase with dilution is taken to indicate that the soln. contains not only $Na^{\cdot}$- and HSO_4'-ions, but there is also an increasing proportion of $H^{\cdot}$- and SO_4''-ions owing to the further ionization of $HSO_4 \rightleftharpoons H^{\cdot}+SO_4''$.

The hydrosulphates taste like acids, and redden litmus. There is probably a partial transformation of the hydrosulphates into the normal sulphates and free acid in aq. soln., *e.g.* $2NaHSO_4=H_2SO_4+Na_2SO_4$; and by dialysis, T. Sabalitschka [29] showed that about 43 per cent. of sodium hydrosulphate and 28·3 per cent. of the potassium salt is transformed in this way. Dil. soln. of potassium hydrosulphate furnish crystals of the normal salt, and four precipitations with alcohol give pure potassium sulphate. So also can normal sodium sulphate be precipitated by alcohol from aq. soln. of the hydrosulphate. Moderately conc. soln. of sodium hydrosulphate deposit crystals which are mainly the normal salt; and hot conc. soln. on cooling give approximately equal parts of the normal and hydrosulphate. E. Mitscherlich showed that above the fusion temp., potassium hydrosulphate behaves in many respects like free sulphuric acid; above its own b.p. it displaces hydrogen chloride from sodium chloride, and attacks many mineral silicates and calcined oxides which are dissolved very slowly at the b.p. of the acid—*e.g.* iron and aluminium oxides, etc. It also forms double sulphates with magnesium, zinc, etc. K. Stammer found the hydrosulphates are reduced to the sulphides when heated to redness in a stream of carbon monoxide, forming carbon and sulphur dioxide, but no sulphur trioxide.

By heating sulphuric acid with sodium hydrosulphate between 200° and 300°, G. F. Brindley [30] obtained crystals of **sodium trihydro-disulphate,** $NaH_3(SO_4)_2$; and C. Schultz, by cooling a soln. of normal sodium sulphate in nearly seven times

its weight of sulphuric acid. H. Lescœur obtained a hydrated salt from a hot soln. of sodium sulphate in three parts of conc. sulphuric acid. C. Schultz's salt melted at 100°, H. Lescœur's at 90°. The latter lost its water at 220°, and this with greater difficulty than the corresponding potassium salt. G. F. Brindley proposed to use this salt as a means of transporting sulphuric acid. The range of stability of $NaH_3(SO_4)_2H_2O$ is indicated in Figs. 47 and 48. J. d'Ans also obtained the complex $Na_2SO_4.4\frac{1}{2}H_2SO_4$, whose range of stability at 25° is indicated in Figs. 47 and 48.

C. Schultz-Sellack,[31] in 1868, found that a salt of the composition $KH_3(SO_4)_2$, that is, $K_2SO_4.3H_2SO_4$, or $KHSO_4.H_2SO_4$—**potassium trihydro-disulphate**—separated from a soln. of normal potassium sulphate in 2 or 3 parts of conc. sulphuric acid; if five parts of acid are used, the soln. requires seeding before the crystals appear. H. Lescœur also, in 1874, obtained a hydrated form. C. Schultz-Sellack's salt, $K_2SO_4.3H_2SO_4.3H_2O$, or $KH_3(SO_4)_2 1\frac{1}{2}H_2O$, forms a cold soln. of potassium sulphate in conc. sulphuric acid. W. Stortenbeker prepared a salt of this same composition by following C. Schultz-Sellack's directions. It was difficult to be quite sure the crystals were free from mother liquor. W. Spring also reported a compound of the same composition, but the water of hydration was a little doubtful. L. Arzalier obtained both $KH_3(SO_4)_2.\frac{1}{2}H_2O$ and $KH_3(SO_4)_2.1\frac{1}{2}H_2O$, and when dried in an inert gas at 150°, both furnished the anhydrous salt, $KH_3(SO_4)_2$. The variability of the water in the reported analyses of this salt also explains the differences in the m.p.—C. Schultz, 95°; H. Lescœur, 61°. The range of stability of $NaH_3(SO_4)_2$ is indicated in the diagrams, Figs. 47 and 48.

W. Spring[32] has also reported some complexes—$6NaHSO_4.H_2SO_4.16H_2O$, and $5NaHSO_4.H_2SO_4.7H_2O$, which in vacuo dried to $5NaHSO_4.H_2SO_4$. F. Bergius also obtained solids corresponding with $Li_2SO_4.7H_2SO_4$, melting about 12°; $Na_2SO_4.8H_2SO_4$, melting about 40°; and $K_2SO_4.6H_2SO_4$, melting about 55°. J. Kendall and M. L. Landon found evidence of $Li_2SO_4.7H_2SO_4$, melting at 13·6°, on the f.p. curve of the two constituents, and likewise also of $2Na_2SO_4.9H_2SO_4$, which is unstable at the m.p., 40°, and transition points to the two modifications of $Na_2SO_4.2H_2SO_4$ at 57° and 58°. J. d'Ans, *vide supra*, also found evidence of $2Na_2SO_4.9H_2SO_4$. W. Spring further reported crystals of a complex $2KHSO_4.3H_2SO_4.3{\cdot}5H_2O$, or $K_2SO_4.4H_2SO_4.3{\cdot}5H_2O$, or $K_2H_8(SO_4)_5.3{\cdot}5H_2O$, which may or may not be a mixture.

E. Mitscherlich[33] and C. F. Rammelsberg prepared a series of double salts of lithium and sodium sulphates from a soln. containing equal mols. of the simple salts. Such a mixture first furnishes large rhombohedral crystals with the composition of **hexahydrated trisodium lithium disulphate,** $Na_3Li(SO_4)_2.6H_2O$, and also of $Na_4Li_2(SO_4)_3.9H_2O$, followed by small crystals of **disodium octolithium sulphate,** $Na_2Li_8(SO_4)_5.2H_2O$. C. F. Rammelsberg prepared small monoclinic crystals of **dipotassium octolithium sulphate,** $K_2Li_8(SO_4)_5.5H_2O$. J. Traube also obtained ditrigonal pyramidal crystals of hydrated trisodium lithium disulphate with axial ratios $a:c=1:0{\cdot}9061$; and, according to A. Johnsen, of sp. gr. 2·009, and negative double refraction. J. Traube and A. Scacchi obtained trigonal crystals of **sodium lithium sulphate,** $NaLiSO_4$, with axial ratios $a:c=1:0{\cdot}5624$, and $\alpha=110°\ 54'$. The crystals exhibited pyroelectrical phenomena; and a positive double refraction. J. Traube also prepared hexagonal prisms or pyramids of **potassium lithium sulphate,** $KLiSO_4$, with axial ratio $a:c=1:1{\cdot}6755$. The salt was investigated by G. Wyrouboff, G. Wulff, J. Traube, and J. Schabus. The crystals have a sp. gr. 2·393; they have a feeble negative double refraction; and the indices of refraction, according to G. Wulff, are for the ordinary and extraordinary rays respectively 1·4697 and 1·4703 with the *C*-line; 1·4715 and 1·4721 with the *D*-line; and 1·4759 and 1·4762 with the *F*-line. The crystals are optically active and exhibit right- and left-handed symmetry. G. Wulff and J. Traube respectively found for plates 1 mm. thick and sodium light, the rotation of the plane of polarization 2·8°–3·0°, and 3·3°–3·8°. E. Doumer found the optical refraction of the soln. to be $\mu=0{\cdot}275$, and the mol. refraction 126·3. C. Spielrein

studied the conditions of equilibrium of mixed soln. of the component salts. G. Wyrouboff prepared hexagonal pyramids of **rubidium lithium sulphate,** $RbLiSO_4$, with axial ratio $a : c=1 : 1\cdot6472$; they have similar properties to the potassium salt.

H. Rose [34] prepared crystals of **tripotassium sodium sulphate,** $3K_2SO_4.Na_2SO_4$, by melting together equal mols. of the two salts; digesting the cold mass with hot water; and cooling the liquid. Crystallization is attended by crystallo-luminescence. A similar result was obtained by melting together potassium sulphate and sodium chloride. J. H. Gladstone, E. Bandrowsky, A. Scacchi, C. F. Rammelsberg, K. von Hauer, J. Mahony, C. J. B. Karsten, and others have also worked on the formation of this salt. F. W. Dupré prepared it by precipitating the magnesia from soln. of kainite, sylvinite, etc., and mixing the clear liquid with sodium chloride. On evaporation, crystals of the double sulphate separate. According to F. Penny, the so-called *plate sulphate*, formerly obtained from kelp, is this double salt. The term *glaserite*—after the alchemist C. Glaser (1664)—was applied by F. L. Hausmann (1847) to native potassium sulphate, found on the lava at Vesuvius, which J. Smithson's analysis (1813) gave as containing 71·4 per cent. of potassium sulphate; 18·6 per cent. of sodium sulphate; 4·6 per cent. of sodium chloride, along with ammonium, copper, and iron chlorides. The term **glaserite** is now applied to the double salt $K_3Na(SO_4)_2$, whose individuality was established by J. H. van't Hoff. Double sulphates containing other proportions of the constituent salts have been reported, but J. H. van't Hoff showed that it is possible to prepare a whole series of solid soln. in which the percentage amount of the contained potassium sulphate varies between 78·6 and 61·8, and such salts are hence to be regarded as representing one solid phase. According to B. Gossner, the double salt crystallizes from soln. of the component sulphates containing $Na_2SO_4 : K_2SO_4$ in a ratio up to 1 : 2. The conditions have been worked out by J. H. van't Hoff and co-workers. R. Nacken's equilibrium diagram of the ternary system K_2SO_4—Na_2SO_4—H_2O, at 34°, is indicated in Fig. 52. *D* represents a soln. sat. with sodium sulphate; *E*, potassium sulphate; *F*, mixed crystals and sodium sulphate; and *G*, potassium sulphate and glaserite; between *HFGI* is the region of mixed crystals; between *IGB*, glaserite. E. Jänecke could not confirm R. Nacken's assumption that a compound of sodium and potassium sulphates is formed in the solid state.

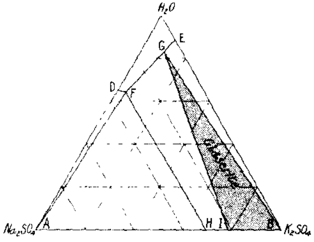


FIG. 52.—Equilibrium Conditions of Ternary System, K_2SO_4—Na_2SO_4—H_2O, at 34°.

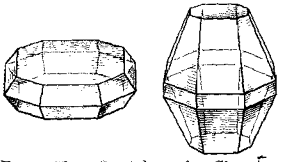


FIG. 53.—Crystals of Glaserite, $K_3Na(SO_4)_2$.

The crystals of glaserite are trigonal or pseudo-trigonal (monoclinic) with axial ratio, according to B. Gossner, $a : c=1 : 1\cdot2904$, and $\alpha=87° 58'$. The typical habit of the crystals with hexagonal symmetry is illustrated by Fig. 53; the first was prepared by W. C. Blasdale at 100°, the second at 50°. This makes it easy to distinguish the crystals of the double salt from those of its components. B. Gossner gives for the sp. gr. 2·697 (15°); J. W. Retgers, 2·695. According to F. Penny, 100 parts of water at 103·5° dissolve 40·8 parts of the salt, which melts at a lower temp. than potassium sulphate. L. Dubrisay studied the temp. of complete miscibility of conc. soln. of potassium and sodium sulphates. C. Spielrein

studied the conditions of equilibrium of mixed soln. of sodium and potassium sulphates.

The ternary system $LiCl-Li_2SO_4-H_2O$ has been studied by F. A. H. Schreinemakers and G. M. A. Kayser.[35] Mixed soln. of sodium sulphate and potassium chloride, and of potassium sulphate and sodium chloride, have been studied qualitatively by F. Rüdorff, C. J. B. Karsten, A. Levol, D. Page, and A. D. Keightley, and G. J. Mulder. The systems were studied by J. H. van't Hoff and L. T. Reicher, who found that the component salts react, forming glaserite, so that $3KCl + 2(Na_2SO_4.10H_2O) \rightleftharpoons K_3Na(SO_4)_2 + 3NaCl + 20H_2O$. A soln. can be prepared sat. with respect to the four solid phases, glaserite, Glauber's salt, potassium chloride, and sodium chloride, at the transition point 3·7°. All the salts indicated in the equation, other than water, represent solid phases. As a result, one pair of the salts—potassium chloride and Glauber's salt—can exist as solid phases in presence of the sat. soln. only below 3·7°, while above that temp., the other pair of salts—glaserite and sodium chloride—can alone exist as solid phases. If the temp. is above the f.p., and ice is accordingly excluded, nine univariant systems, with three solid phases, are theoretically possible. W. Meyerhoffer and A. P. Saunders have studied this system in more detail, and the transition temp. was found to be 4·4°, not 3·7°; they worked at 0°, 4·4°, 16°, and 25°; W. C. Blasdale followed up the work at 50°, 75°, and 100°. W. C. Blasdale's experimental data for 0°, 25°, and 50° expressed in eq. mols. of the various salts per 1000 mols. of water, are plotted in Figs. 54 to 56, with respect to four axes representing the four component salts—K_2Cl_2, Na_2Cl_2, Na_2SO_4, and K_2SO_4—and the various points are connected by straight lines, although these lines should probably be curved.

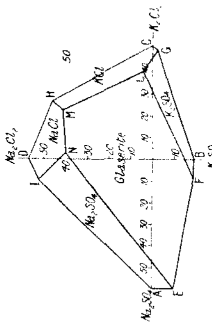


Fig. 56.

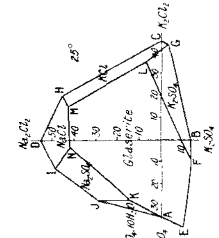


Fig. 55.

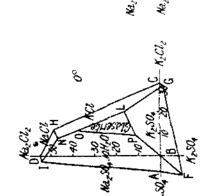


Fig. 54.

Equilibrium Diagram of Aqueous Solutions of Sodium and Potassium Chlorides and Sulphates at 0°, 25°, and 50°.

The diagram actually represents the horizontal projection of a solid figure. Any point on it may represent a number of soln. of different composition, but if perpendiculars are erected at the limiting points and given lengths proportional to the total number of mols. present in the sat. soln. to which these points correspond, and if the ends of these perpendiculars are properly connected, any point which appears on the planes which limit the resulting solid figure can have a single definite value only.

The diagram indicates the composition of all possible soln. which can be in equilibrium with the six different solid phases: *viz.* glaserite, Glauber's salt, sodium chloride, sodium sulphate, potassium chloride, and potassium sulphate.

W. C. Blasdale has applied these results to show what takes place during the fractional crystallization by the evaporation of soln. containing different proportions of the component salts—the separation of (i) sodium and potassium chlorides; (ii) potassium chloride and sulphate; (iii) potassium and sodium sulphate; (iv) sodium sulphate and chloride; and of (v) potassium salts from mixtures of sodium and potassium chlorides and sulphates. The results were then extended to samples of desert brine. J. H. Hildebrand also showed how J. H. van't Hoff's results show the course of the fractional crystallization of sea-water containing magnesium, sodium, and potassium sulphates and chlorides.

Table XL.—Composition of Saturated Solutions in Equivalent Mols. per 1000 Mols. of Water.

Points in Fig.	Sat. with	Na_2Cl_2	K_2Cl_2	Na_2SO_4	K_2SO_4	Sp. gr.
	0° (Fig. 54).					
A	Na_2SO_4	—	—	5·85	—	1·043
B	K_2SO_4	—	—	—	7·47	1·063
C	KCl	—	34·05	—	—	1·153
D	NaCl	53·84	—	—	—	1·206
F	Glauber's salt and K_2SO_4	—	—	7·99	9·30	1·118
G	K_2SO_4 and KCl	—	33·66	—	1·25	—
H	NaCl and KCl	48·58	12·75	—	—	—
I	NaCl and Glauber's salt	53·28	—	2·32	—	1·185
L	K_2SO_4, KCl, glaserite	19·41	21·48	2·87	—	1·188
N	NaCl, Glauber's salt, KCl	49·44	9·43	—	3·75	1·240
O	KCl, Glauber's salt, glaserite	41·71	12·15	—	3·35	1·232
P	K_2SO_4, Glauber's salt, glaserite	11·50	16·00	6·0	—	—
	25° (Fig. 55).					
A	Na_2SO_4	—	—	35·41	—	1·212
B	K_2SO_4	—	—	—	12·46	1·088
C	KCl	—	44·62	—	—	1·187
D	NaCl	54·90	—	—	—	1·199
E	Na_2SO_4 and glaserite	—	—	39·27	9·63	1·282
F	K_2SO_4 and glaserite	—	—	8·48	13·69	1·149
G	K_2SO_4 and KCl	—	44·11	—	1·50	1·190
H	KCl and NaCl	46·04	19·66	—	—	1·237
I	NaCl and Na_2SO_4	49·56	—	12·44	—	1·239
J	Na_2SO_4 and Glauber's salt	29·00	—	27·5	—	1·243
K	Na_2SO_4, Glauber's salt, glaserite	21·92	—	28·25	7·57	1·273
L	KCl, K_2SO_4, glaserite	10·45	35·49	—	2·30	1·200
M	KCl, NaCl, glaserite	43·08	19·78	4·45	—	1·250
N	NaCl, Na_2SO_4, glaserite	53·75	—	2·85	11·40	1·266
	50° (Fig. 56).					
A	Na_2SO_4	—	—	56·86	—	1·301
B	K_2SO_4	—	—	—	17·60	1·110
C	KCl	—	52·10	—	—	1·198
D	NaCl	56·24	—	—	—	1·188
E	Na_2SO_4 and glaserite	—	—	58·00	9·72	1·351
F	K_2SO_4 and glaserite	—	—	8·61	17·95	1·307
G	KCl and K_2SO_4	—	51·03	—	1·90	1·212
H	KCl and NaCl	44·82	26·61	—	—	1·246
I	NaCl and Na_2SO_4	51·93	—	9·26	—	1·223
L	K_2SO_4, KCl, glaserite	7·21	42·36	—	2·67	1·203
M	KCl, NaCl, glaserite	41·36	27·01	4·00	—	1·254
N	NaCl, Na_2SO_4, glaserite	40·15	14·58	11·74	—	1·248

B. Karandéeff found that the fusion curves of the system $KF-K_2SO_4$ gave eutectics at 883° (41 mols. per cent. of potassium fluoride), and 788° (83 mols. per

cent. of potassium fluoride). There is a maximum at 887° corresponding with the *m.p. of potassium fluosulphate*, $K_2SO_4.KF$, which decomposes below 578°. R. F. Weinland and J. Alfa[36] prepared feebly doubly-refracting monoclinic sphenoidal crystals of monohydrated **tripotassium difluorodisulphate,** $K_3H\,S_2O_7F_2.H_2O$, by evaporating soln. of potassium sulphate or hydrosulphate with 40 per cent. hydrofluoric acid. H. Zirngiebl found the crystals to have the axial ratios $a:b:c=1{\cdot}0130:1:0{\cdot}8218$, and $\beta=108°\ 39'$. C. Pape's *dipotassium sodium chlorosulphate*, $K_2SO_4.NaCl$, was probably a mixture. O. Ruff and W. Plato found that mixtures of sodium sulphate with sodium chloride or bromide give the V-fusion curve with eutectics respectively at about 650° (46 mols. per cent. of sodium sulphate), and at 640° (38 mols. per cent. of sodium sulphate); while mixtures of potassium sulphate with potassium chloride or iodide give the V-fusion curve with eutectics respectively at 720° (25 mols. per cent. potassium sulphate) and 670° (13 mols. per cent. potassium sulphate). E. Jänecke has confirmed these results. H. Rose obtained a transparent mass during the absorption of sulphur trioxide by potassium chloride, which, according to C. Schultz-Sellack, has the composition $KCl.8SO_3$, and which A. W. Williamson and H. Schiff called *potassium chlorosulphate*. According to S. Zinno, iodine reacts with potassium sulphite, forming *potassium iodosulphate*, $K_2SO_3I_2$, in six-sided columns isomorphous with potassium sulphate. J. C. G. de Marignac obtained what were thought to be trigonal crystals of **trisodium fluorosulphate,** $Na_2SO_4.NaF$, in the preparation of sodium fluoride with hydrofluoric acid contaminated with sulphuric acid. The three-component system, $NaCl—Na_2SO_4—H_2O$, was investigated by W. Meyerhoffer and A. P. Saunders during their study of the effect of foreign salts, when it was found that the change from Glauber's salt to anhydrous sodium sulphate is reduced from 32·8° to 17·9°, when the liquid is sat. with sodium chloride. The system has also been studied by J. H. van't Hoff, A. W. Browne, A. Seidell, and by F. K. Cameron, J. M. Bell, and W. O. Robinson. The general results at 25° are indicated in Fig. 57, which represents a portion of the triangular diagram with Na_2SO_4 at the top apex, NaCl at the right apex, and H_2O at the left apex. The curve *AB* represents the soln. in equilibrium with the solid phase $Na_2SO_4.10H_2O$; *BC*, with the solid phase Na_2SO_4; and *CD*, with the solid phase NaCl. There is thus no sign of a double salt. F. A. H. Schreinemakers and G. M. A. Kayser investigated the ternary system, $Li_2SO_4—LiCl—H_2O$.

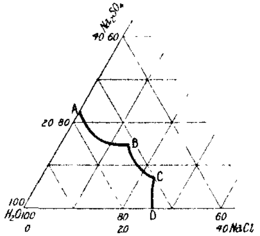
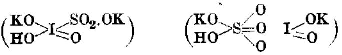


FIG. 57.—Ternary System, NaCl—Na_2SO_4—H_2O, at 25°.

J. C. G. de Marignac prepared monohydrated **trisodium nitratosulphate,** $Na_2SO_4.NaNO_3.H_2O$, by evaporating mixed soln. of the component salts. The crystals were monoclinic prisms corresponding with the mineral *darapskite* which, according to A. Osann, have the axial ratios $a:b:c=1{\cdot}5258:1:0{\cdot}7514$, and $\beta=102°\ 25'$, and sp. gr. 2·203; A. de Schulten found the sp. gr. to be 2·197. There is also the mineral *nitroglauberite*, $2Na_2SO_4.6NaNO_3.3H_2O$. J. C. G. de Marignac also prepared **dipotassium hydroiodatosulphate,** $KHSO_4.KIO_3$, in monoclinic prisms with the axial ratios $a:b:c=1{\cdot}9288:1:1{\cdot}0346$, and $\beta=93°\ 14'$. The compound was studied by G. S. Sérullas, N. A. E. Millon, and C. F. Rammelsberg. The constitutional formula was denoted respectively by C. W. Blomstrand and C. Friedheim:



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§ 27. Ammonium Sulphates

A. Libavius mentioned that crystals of a compound are formed when *spiritus urinæ* is treated with oil of vitriol, and the soln. evaporated. J. R. Glauber also made this salt by treating volatile alkali with sulphuric acid, and he pointed out some of its medicinal uses. For a time this salt was known as *sal ammoniacum secretum Glauberi*. D. L. G. Karsten,[1] M. Sage, L. Palmieri, and O. Popp found ammonium sulphate occurring as *mascagnite* about volcanoes in the fissures of lava, as at Vesuvius, Etna, and the Lipari Islands; C. Schmidt and O. Popp, in the boric acid fumoroles of Tuscany, etc.; F. H. Storer, in anthracite coal; etc. S. D. Crenshaw found ammonium sulphate in the flue dust of kilns, using Pennsylvanian anthracite as fuel; A. Müntz and E. Lainé, from the dry distillation of turf; R. E. Carpenter and S. E. Linder, among the reaction products of Claus' kiln; E. Berglund, among the products of the hydrolysis of imidosulphonic acid; etc.

Ammonium sulphate is produced when aqua ammonia, or ammonium carbonate, is neutralized with sulphuric acid, a reaction studied by F. C. Hills, R. W. Wallace, P. S. Brown, P. Spence, and T. Illingworth, etc. L. Mond treated ammonium chloride with sulphuric acid until all the hydrogen chloride was expelled, and then converted the resulting hydrosulphate, $(NH_4)HSO_4$, with ammonia so as to convert it into the normal sulphate. P. de Lachomette made it by the oxidation of crystallized ammonium sulphite; and H. H. Stephens, by treating putrefied ammonia with calcium, sodium, or ferrous sulphate, or with alum. W. Leybold, K. Zimpell, O. Kausch, H. Ost, and many others have studied the preparation of ammonium sulphate on a manufacturing scale. H. Hampel has described two continuous processes for manufacturing ammonium sulphate from the sulphates of the potassium salts available at Stassfurt, etc. The one process involves reactions which are illustrated by the equation: $K_2SO_4+Ca(NO_3)_2=2KNO_3+CaSO_4$; $CaSO_4+2NH_3+CO_2+H_2O=CaCO_3+(NH_4)_2SO_4$; and $CaCO_3+2HNO_3=Ca(NO_3)_2+CO_2+H_2O$. Synthetic ammonia and nitric acid are utilized, and the by-product, potassium nitrate, is more valuable than the ammonium sulphate. The other process is likewise illustrated by the equations: $MgSO_4+CaCl_2=MgCl_2+CaSO_4$; $CaSO_4+2NH_3+CO_2+H_2O=CaCO_3+(NH_4)_2SO_4$; $CaCO_3+2HCl=CaCl_2+H_2O+CO_2$; $MgCl_2+H_2OMgO+2HCl$. D. H. B. Wride has also discussed the manufacture of ammonium sulphate from calcium sulphate, ammonia, and carbon dioxide. K. Nishizawa studied the equilibrium of the five component system involving Na_2SO_4, $NaHSO_4$, $(NH_4)_2SO_4$, NH_4HCO_3, and H_2O, at 15°, in order to find the best conditions for the manufacture of ammonium sulphate from sodium sulphate by the ammonia-soda process. He found for each 1000 grms. of water, 79·54 mols of Na_2SO_4 and 134·2 mols of NH_4HCO_3 should be mixed, and there will be produced 45·82 mols of Na, 20·90 mols of HCO_3, 79·54 mols of SO_4, and 134·2 mols of NH_4 per 1000 mols of water at 15°.

In W. Feld's process, a mixture of hydrogen sulphide and ammonia is passed into aq. soln. of ammonium tri- and tetra-thionate whereby the polythionates are converted into thiosulphate: $(NH_4)_2S_3O_6+(NH_4)_2S=2(NH_4)_2S_2O_3$; and $(NH_4)_2S_4O_6+(NH_4)_2S=2(NH_4)_2S_2O_3+S$. The latter is treated with sulphur dioxide and re-converted into polythionate, but double the amount is obtained as was originally employed: $2(NH_4)_2S_2O_3+3SO_2=(NH_4)_2S_3O_6+(NH_4)_2S_4O_6$. The

excess of polythionate is removed, and the soln. boiled whereby ammonium sulphate, sulphur dioxide, and sulphur are produced: $(NH_4)_2S_3O_6=(NH_4)_2SO_4+SO_2+S$. The sulphur dioxide is utilized as indicated above, and likewise also the sulphur which is burnt to sulphur dioxide. The reactions have been studied by F. Raschig.

In 1781, Earl of Dundonald patented a process for the recovery of volatile alkali produced in the distillation of coal, but nothing came of it; then followed, in 1837, the patent of G. D. Midgley and J. H. Kyan for the treatment of gas liquor for its ammonia. Ammonium sulphate was once prepared by saturating raw gas liquor directly with sulphuric acid until the yellow liquid had a milky appearance. The neutral soln. so formed was evaporated until the salt crystallized out. The product was generally yellow or grey, and sometimes red or blue. It contained other ammonium salts—sulphite, chloride, thiocyanate, etc.—as impurity. The impure sulphate had a much lower market value than a purer product, and the cost of the fuel required for the evaporation rendered the process not satisfactorily remunerative. The salt is now made by boiling ammoniacal soln. like gas liquor with lime, and passing the ammonia which is evolved into sulphuric acid. At first, the ammonia was generated in a simple boiler heated by a direct fire, but the wear of the boiler and scale produced by the formation of a hard incrustation of lime were so troublesome that improvements were soon introduced. Among the first. was the use of steam for heating the still in which the ammonia was generated. The steam was either blown directly into the liquor, or passed through coils placed in the liquor; then a combination was so arranged that a boiler at a higher level was heated by steam from a boiler at a lower level. The volatile products were driven from the upper boiler, and the lime treatment was conducted in the lower boiler. As soon as the liquid in the lower boiler was exhausted, it was run off, and the liquor from the upper boiler passed into the lower boiler, where it was treated with lime. The upper boiler was filled with fresh liquor, which was heated by the steam from the lower boiler. The cycle was repeated anew.

In modern continuous processes, based on the use of A. Coffey's still, the *ammoniacal liquor is run into a superheater, where it is heated previous to entering* the still. The hot liquor is mixed with lime and passed down a tower with tiers of chambers—*vide* Fig. 66. A strong current of steam is blown in at the bottom of the tower and passed upwards through perforated caps in the floor of each chamber. Fresh liquor enters at the top of the tower, and the exhausted liquor passes away at the bottom. The gases charged with ammonia pass from the top of the tower and are led through sulphuric acid in the *saturator*, where the ammonia is absorbed. The unabsorbed carbon dioxide, hydrogen sulphide, etc., pass along to the superheater, where they give up a large portion of their heat. This heat is utilized to warm up the gas liquor on its way to the tower. The gases may then pass on to the chimney, or they may be treated in an iron oxide purifier or in a Claus' kiln. The ammonium sulphate which crystallizes from the sat. sulphuric acid is allowed to drain. There are several different types of plant on the market—*e.g.* Savalle's, Feldmann's, Grüneberg and Blum's, etc.

The early analyses of R. Kirwan, and of J. J. Berzelius, translated into modern notation would be represented by $(NH_4)_2SO_4.H_2O$; but later analyses by A. Ure, E. Mitscherlich, O. B. Kühn, etc., indicate no water of crystallization. The commercial salt is light grey and may be guaranteed to contain at least 24 per cent. NH_3; *it commonly contains a little more—say, 24·25 to 24·75 per cent.* NH_3—from 2 to 4 per cent. of moisture; and from 0·15 to 0·4 per cent. of free sulphuric acid—theory for $(NH_4)_2SO_4$, 25·76 per cent. NH_3, 74·24 per cent. H_2SO_4. The salt is used as a fertilizer, and buyers stipulate that the salt shall be free from cyanides which act deleteriously on vegetable growths. When the colour is good, and the moisture low, the sulphate may be sold as "white" when the required minimum is 25·25 per cent. NH_3. H. Fleck found samples of commercial crude ammonium sulphate with 0·5 grm. of arsenic per kilogram.

The properties of ammonium sulphate.—Ammonium sulphate can be obtained in well-developed transparent **crystals** by evaporation in cold dry weather under atm. press. of sat., not supersaturated, soln. The crystals belong to the rhombic system, and, according to E. Mitscherlich,[2] have the axial ratios $a:b:c$ $=0.5643:1:0.731$; or, according to A. E. H. Tutton, $0.5635:1:0.7319$. The crystals are isomorphous with potassium sulphate, not only morphologically, but also in the continuous variation in the physical properties of mixed crystals as shown by G. Wyrouboff and E. Mallard for the optic axial angles, and by J. W. Retgers for the sp. gr. In the series of isomorphous alkali sulphates, A. E. H. Tutton found ammonium sulphate to fall between rubidium and cæsium sulphates with respect to solubility, mol. vol., refractive index, axial ratios, etc. A. Fock has also investigated the equilibrium conditions of the mixed crystals with water, and found the composition of the soln. changed continuously with the composition of the solid phase. A. Ogg and F. L. Hopwood have calculated the dimensions of the unit rhomb of the crystals of ammonium sulphate from the **X-radiograms**, and found the lengths of the sides a, b, c of the unit rhomb to be respectively 5.951×10^{-8} cm.; 10.560×10^{-8} cm.; and 7.729×10^{-8} cm.; while the volume is 485.71×10^{-24} cc. There are four mols. in the elementary cell. On comparison with the corresponding values for the isomorphic sulphates of potassium, rubidium, and cæsium, and remembering that the replacement in the elementary cell of eight atoms of potassium by forty atoms of the four radical groups NH_4 causes no more distension of structure than if eight atoms of rubidium had replaced the eight atoms of potassium; and the replacement of eight atoms of potassium by eight atoms of cæsium causes twice the distension produced by forty atoms of the form NH_4-radicles. This is taken as a conclusive proof against the theory of crystal structure based on the closest packing of the constituent atoms, and of their spheres of influence.

The earliest determination of the **specific gravity** of ammonium sulphate is 1·7676 by le citoyen J. H. Hassenfratz[3] at Paris in 1798. The other published data range from 1·75 reported by H. Buignet to 1·773 reported by H. G. F. Schröder. The best representative value must be near 1·7687, as reported by A. E. H. Tutton at 20° (water at 4° unity). The mol. vol. by A. E. H. Tutton is 74·63; and P. A. Favre and C. A. Valson find the eq. volume of the salt is 37·4 c.c. W. Spring gives the following values for the sp. gr. of the salt at different temp. and for the volume assumed at different temp. by unit volume of the salt at 0°:

	0°	10°	20°	40°	60°	80°	100°
Sp. gr. . .	1·7763	1·7748	1·7734	1·7703	1·7667	1·7617	1·7567
Volume . .	1·000000	1·000846	1·001667	1·003391	1·005431	1·008289	1·011191

W. Spring found an anomalous change in the sp. gr. of ammonium sulphate by compression at 20,000 atm., but J. Johnston and L. H. Adams could detect no change at 12,000 atm. provided the crystals are homogeneous and free from holes and cracks. A. Michel and L. Krafft[4] found the sp. gr. of aq. soln. sat. at 15° to be 1·248; A. E. H. Tutton gives 1·2030 for the sp. gr. at 20° of a 35 per cent. aq. soln.—water at 4° unity. H. Schiff found at 19°:

Per cent. $(NH_4)SO_4$.	1	5	10	15	20	25	30	40	50
Sp. gr. .	1·0057	1·0287	1·0575	1·0862	1·1149	1·1439	1·1724	1·2284	1·2890
Mol. vol. .	57·2	58·4	60·3	62·3	64·1	67·4	70·7	72·9	

The **molecular volumes** are by J. Traube, who also gave 74·5 for a 100 per cent. soln. J. A. Groshans has also studied the mol. vol. of these soln. Further data were given by C. A. Valson, S. de Lannoy, F. Kohlrausch, and R. Abegg, etc. P. A. Favre and C. A. Valson gave 1·0378 for the sp. gr. of a normal soln. at 20°; and for the **specific volume** of a normal soln. at 0°, 15°, and 30°, W. Lerche gives 1·000000, 1·00241, and 1·00661 respectively. S. de Lannoy gave for the sp. vol. v of 4 per cent. soln., when v_0 is the sp. vol. of the soln. at 0°, $v=v_0(1-0.0000048\theta$

$+0\cdot000004640\theta^2$) between 0° and 40°, and $v=v_0(1-0\cdot00010590\theta+0\cdot000000332\theta^2)$ between 40° and 82°; for 12 per cent. soln., $v=v_0(1-0\cdot0001723\theta+0\cdot000002837\theta^2)$ between 0° and 40°, and $v=v_0(1-0\cdot0001865\theta+0\cdot0000002480\theta^2)$ between 40° and 85°; for 20 per cent. soln., $v=v_0(1-0\cdot0002424\theta+0\cdot000001720\theta^2)$ between 0° and 82°; and for 50 per cent. soln., $v=v_0(1-0\cdot00026900\theta+0\cdot000000752\theta^2)$ between 0° and 93·7°. D. Dijken and A. Kanitz also made observations on the sp. vol. of soln. of ammonium sulphate; and O. Pulvermacher on the sp. gr. of these soln. S. de Lannoy gave −5·1° for the temp. of **maximum density** of a 1 per cent. soln., −30·3° for a 12 per cent. soln.; −70·4° for a 20 per cent. soln., and −178° for a 50 per cent. soln. P. A. Favre and C. A. Valson found that during the soln. of an eq. of ammonium sulphate in a litre of water, the water contracts 27·3 c.c., and the contraction of the salt amounts to 10·1 c.c., so that the total contraction is 37·4 c.c. H. Gilbault found that at 20°, *w* grms. of the salt dissolved in 100*w* grms. of water contracted such that if *V* denotes the volume of the soln., when v_1 is the volume of the water and v_2 that of the salt, v_1+v_2-V, 0·1120, 0·0835, 0·0583, and 0·0343, when *w* is respectively 10, 20, 30, and 40. The subject is also discussed by W. Ostwald and M. Rogow.

According to W. Spring,[5] after subjecting ammonium sulphate to a press. of 20,000 atm. for three weeks the press. fell from 1·773 (20°) to 1·750 (22°); and after a repetition of the treatment the sp. gr. was 1·760 (22°). W. C. Röntgen and J. Schneider give 0·741 and 0·853 for the relative **compressibility** of a soln. of a mol. of the salt in 1,500 and 700 mols. of water respectively; and for the relative mol. compressibility 0·808 and 0·887 respectively. P. G. Tait also measured the compressibility of soln. of ammonium sulphate. H. Gilbault found that if *a* denotes the quotient: mol. of ammonium sulphate by mol. of water; *D* the sp. gr. of the soln. at 20° (water at 4° unity); *k* is the mean, and *β* the mol. compressibility, then for *w* per cent. soln. at 20° the value of $(\log k_0-\log k)D/a$ is nearly constant.

TABLE XLI.—COMPRESSIBILITY OF SOLUTIONS OF AMMONIUM SULPHATE.

w	*a*	*D*	*k*	*β*	Constant.
0	0	1	4437	4437 (β_0)	—
10	0·02941	1·0575	3958	4036	1·4773
20	0·06383	1·1140	3479	3652	1·4766
30	0·10465	1·1724	3006	3279	1·4711
40·112	0·15445	1·2290	2522	2897	1·4726

Water with ammonium sulphate in soln. has a smaller sp. vol. than water. From P. G. Tait's measurements of the press. necessary to produce a corresponding contraction in the sp. vol. of water, G. Tammann calculated that the increase in the internal press. *P* atm. of water produced by the dissolution of the salt expressed in grams of salt per 100 grms. of water, is as follows:

Grm. salt	3·34	6·78	14·0	30·19
Internal press. δP, at 10°	243	448	759	1158
„ „ 15°	250	455	755	—
„ „ 30°	247	435	732	—

C. A. Valson gave 59·7 mm. for the **capillary rise** in a tube 0·5 mm. diameter at 20°. The **surface tensions** of a mol. of the salt in 1500 and 700 mols. of water may be regarded as proportional to the product of the capillary rise and sp. gr., and they were given by W. C. Röntgen and J. Schneider as 116·91 and 113·99 respectively. H. Sentis has also studied the surface tension of ammonium sulphate soln. C. Forch found the surface tension *σ* (mgrm. per mm.) of soln. at *θ*° containing *m*=half a mol. per litre:

TABLE XLII.

m	θ	σ	$\omega=\sigma_{soln.}-\sigma_{water}$	ω/m
5·285	15·0	8·565	0·749	0·142
4·100	15·8	8·351	0·547	0·134
3·180	15·4	8·229	0·419	0·132
2·135	15·3	8·089	0·278	0·131
1·274	15·2	7·984	0·171	0·134
1·061	14·9	7·966	0·149	0·140
0·881	15·1	7·939	0·125	0·142

A. Kanitz gave the **viscosity** of N-, $\frac{1}{2}N$-, $\frac{1}{3}N$-, and $\frac{1}{4}N$-soln. as respectively 1·1114, 1·0552, 1·0302, and 1·0148 (water unity). A. Kanitz also measured the viscosity of soln. of ammonium sulphate mixed with potassium or aluminium sulphate. R. Abegg and O. Pulvermacher have also studied the viscosity of soln. of this salt. T. Graham found that in 24 hrs. 0·0389 grm. diffused from an approximately normal soln. into water—J. H. Long found 0·0482 grm. J. H. Long also found the **velocity of diffusion,** *i.e.* the relative number of mols. which diffused from a normal soln. in a day, to be 724.

The **coefficient of thermal expansion** of the solid salt can be computed from W. Spring's data indicated above, and A. de Lannoy found for 4 per cent. soln. at 50°, 0·0004374; at 100°, 0·0007099; for 12 per cent. soln., 0·000434 at 50°, and 0·000682 at 100°; for 20 per cent. soln., 0·000414 at 50°, and 0·000586 at 100°; and for 50 per cent. soln., 0·000344 at 50°, and 0·000419 at 100°. He also represents his results by a formula of the type $v=v_0(1+a\theta+b\theta^2)$ as indicated above. G. Tammann's value for the **specific heat** of the solid salt is 34 Cals. per mol J. C. G. de Marignac gives for the sp. ht. of soln. $(NH_4)_2SO_4+nH_2O$ at 19·51°.

n	15	25	50	100	200
Sp. ht.	0·7385	0·8030	0·8789	0·9930	0·9633
Mol. ht.	297	476·3	907	1802	3595

G. Tammann, A. Winkelmann, and J. Thomsen also give values for this constant.

According to R. F. Marchand,[6] the **melting point** of ammonium sulphate is 140°; but this is wrong, for it really referred to the hydrosulphate; at 280° the salt is said to begin to vaporize, and at the same time to be decomposed with the formation of some nitrogen and of ammonium sulphite. On a gradually rising temp., W. Smith found that the evolution of ammonia could be detected between 120° and 125°, and in some cases at as low a temp. as 80°. R. Reik says that the sublimation in vacuo as well as at ordinary temp. is attended by a transformation of the salt into the hydrosulphate, $(NH_4)HSO_4$. W. Smith showed that the observed fusion is not due to the melting of the normal sulphate, for this salt does not melt but passes into the hydrosulphate, and a very pure hydrosulphate can be obtained by heating the normal sulphate to about 320° in a platinum dish. Ammonia is first evolved, and as the temp. rises, ammonium sulphites are formed, and finally ammonia, sulphurous oxide, water, and nitrogen escape. The residue left behind on cooling is almost pure NH_4HSO_4. At the higher temp., the ammonia mol. and that of sulphur trioxide mutually decompose each other, forming nitrogen, sulphur dioxide, and water. However, ammonium sulphate at this high temp. decomposes, so that the hydrosulphate remains as a residue. P. Schweitzer believed that the hydrosulphate is formed when normal ammonium sulphate is heated, and at a higher temp. he supposed that the product is *diammonium tetrahydrotrisulphate*, $(NH_4)_2H_4(SO_4)_3$, while at a rather lower temp., *tetrammonium dihydrotrisulphate*, $(NH_4)_4H_2(SO_4)_3$, is formed. S. W. Johnson and R. H. Chittenden appear to regard these salts as mixtures of ammonium hydrosulphate and pyrosulphate. H. Schulze found that the pyrosulphate is formed by a prolonged heating between 250° and 300°. E. Jänecke obtained 251° for the m.p. of the

hydrosulphate, and 357° for the simultaneous melting and decomposition of the normal salt under atm. press. Owing to the decomposition of the normal sulphate in open tubes, it is impossible to determine the m.p. under these conditions. G. Bartha observed that ammonium sulphate decomposes at 200° in vacuo before volatilizing. C. Caspar obtained with an open tube a softening of ammonium sulphate at 310°, a melting at 336°–339°, and a decomposition at 355° ; and with a closed tube, a softening at about 360°, and a melting at 417°–423°. The m.p. is probably much higher than is usually supposed because J. Kendall and M. L. Landon did not succeed in melting the normal salt in a sealed tube at the b.p. of sulphur—about 445°—but J. Kendall and A. W. Davidson found that in a closed tube, under an ammonia press. greater than atmospheric, the salt begins to soften at 490°, and melts at 513°±2°. It is a unique example in inorganic chemistry, of a sulphate with a m.p. below that of the corresponding chloride, which melts at 550° under a press. of approximately 66 atm. Usually the chlorides melt at a lower temp. than the sulphates.

G. T. Gerlach measured the **boiling points** of soln. of different conc. with 15·1, 58·0, and 115·3 grms. of salt per 100 grms. of water, the b.p. are 101°, 104°, and 108·2° respectively; at 108·2° the solid phase is $(NH_4)_2SO_4$. This subject has also been investigated by S. M. Johnston. C. Matignon and F. Meyer found the b.p. of a sat. soln. of ammonium sulphate is 108·9°, and the soln. contains 3·922 mols. per 1000 grms.; and a soln. sat. with both sodium and ammonium sulphates boils at 111°, and contains 1·125 mols. of the former salt and 3·175 mols. of the latter per 1000 grms. of soln. H. Lescœur's value for the maximum **vapour pressure** of a sat. soln. is 14·8 mm. at 20°. F. M. Raoult found the lowering of the vap. press. of a 1 per cent. soln. to be $0·230\times7·6$; and G. Tammann, for the lowering of the vap. press. of soln. of different conc. at different temp. Soln. with 5·18, 43·53, and 79·95 grms. of salt per 100 grms. of water, at 100°, lowered the vap. press. 8·4, 75·9, and 141·0 mm. respectively. Soln. with 13·93 and 40·91 grms. of salt in 100 grms. of water lowered the vap. press. of water:

	32°	52°	67°	76·3°	88°	93°	101°
Soln. 13·93 grms. .	1·0	5·2	6·7	9·9	14·5	19·9	24·3 mm.
Soln. 40·91 grms. .	3·5	10·3	2·9	30·4	46·2	58·0	70·8 mm.

L. C. de Coppet found that the **freezing point** of a sat. soln. of the salt, containing 62·2 grms. of salt in 100 grms. of water, is −19·05°; and, according to F. Guthrie, when soln. of different conc. are cooled, the solid phase separating at different temp. is as follows:

Per cent. $(NH_4)_2SO_4$.	10	20	40	41·7	41·9	43·2
Separation at . .	−2·6°	−6·0°	−16°	−17°	0°	19·0
Solid phase . .		Ice		Eutectic	$(NH_4)_2SO_4$	

The lowering of the f.p. of water by the dissolution of the salt has been investigated by L. C. de Coppet, F. Rüdorff, F. M. Raoult, and by H. C. Jones and his co-workers A gram of the salt in 100 c.c. of water lowers the f.p. 0·276° (L. C. de Coppet), 0·269° (F. Rüdorff), and F. M. Raoult gives the lowering of the f.p. of a 1 per cent. soln. as 0·273°, and he gives the mol. lowering of the f.p. as 37·0°, when L. C. de Coppet gives 36·4°. H. C. Jones and C. G. Carroll measured the effect of ammonium sulphate on the f.p. of soln. of hydrogen peroxide and found the depression of the f.p. to be smaller than with water: and it was therefore assumed that a complex is formed by hydrogen peroxide and ammonium sulphate.

M. Berthelot's [7] value for the **heat of formation** of ammonium sulphate, $(NH_4)_2SO_{4solid}+2NH_{3gas}=(NH_4)_2SO_4+67·6$ Cals. J. Thomsen gives 65·25 Cals. The former also gives $2NH_3aq+H_2SO_4aq=29·06$ Cals., and the latter, 29·06 Cals. The rise in the thermal value of the reaction, $SO_3.200H_2O+2NH_4OH.200H_2O=(NH_4)_2SO_4.401H_2O+27·79+0·069\theta$, where θ denotes the temp. The **heat of neutralization** of a mol. of ammonia with an eq. amount of sulphuric acid, is 14·1 Cals.

(J. Thomsen), 14·5 Cals. (M. Berthelot). J. Thomsen gives −2·37 Cals. for the **heat of solution** of a mol. of the salt in 400 mols. of water at 18°, and in 200 mols. of water, −2·33 Cals. The **heat of dilution** of a soln. of a mol. of the salt in 10 mols. of water with *n* more mols. of water, according to J. Thomsen, is −0·253 Cal. when $n=30$; −0·437 Cal. when $n=50$; −0·632 Cal. when $n=100$; and −0·750 Cal. when $n=200$. M. Berthelot gives −2·7 Cals. for the heat of soln. of one part of the salt in 50 to 100 parts of water. According to C. M. van Deventer and H. J. van de Stadt, the heat of soln. of a mol. in 200 mols. of water is −3·3 Cals., the theoretical heat of soln. is −1·5 Cals., and the integral heat of soln., −1·3 Cals.; P. A. Favre and C. A. Valson give the heat of soln. of a gram-eq. of the salt in a litre of water at 19·65° as −0·979 Cal., at 24·20°, −0·936 Cal., and at 28·4°, −0·996 Cal. The heat of soln. of a gram-eq. of the salt in 147 gram-eq. of water is 0·981 Cal.; if the water contains an eq. of sulphuric acid, −1·977 Cals.; and if five eq. of this acid, −2·471 Cals.; if one eq. of hydrochloric acid, −3·054 Cals., and if five eq., −3·071 Cals. P. Chroustschoff studied the heat of soln. of ammonium sulphate in soln. of potassium chloride. M. Berthelot and P. A. Favre and C. A. Valson have studied the behaviour of mixtures of ammonium sulphate with other salt soln.—potassium nitrate, chloride, carbonate and hydrocarbonate, and sodium diborate, for instance, $2(NH_4)_2SO_4+KNO_3=-0·101$ Cal.; $KCl=0·000$ Cal.; $\frac{1}{2}K_2CO_3=-3·18$ Cals.; $KHCO_3=-0·12$ Cal.; $\frac{1}{4}Na_2B_4O_7=-2·25$ Cals.; $\frac{1}{2}BaCl_2=3·279$ Cals. M. Berthelot says that G. H. Hess's law of thermo-neutrality is not clear with ammonium sulphate. P. A. Favre has also measured the heat of reaction of ammonium sulphate and barium chloride.

M. Erofejeff[8] found the **refractive indices** of ammonium sulphate for lithium and sodium light for vibrations parallel to all three axes; and A. E. H. Tutton found for the α, β, and γ indices of refraction, where the vibrations are respectively parallel to the *c*, *b*, *a* axes, at ordinary temp., say 15°:

		Li-line.	*C*-line.	*Na*-line.	*Tl*-line.	*F*-line.	*G*-line.
15°	α-index	1·5177	1·5182	1·5209	1·5237	1·5370	1·5318
	β-index	1·5199	1·5204	1·5230	1·5258	1·5291	1·5340
	γ-index	1·5297	1·5302	1·5330	1·5359	1·5394	1·5445
80°	α-index	1·5146	1·5151	1·5178	1·5206	1·5239	1·5387
	β-index	1·5174	1·5179	1·5205	1·5233	1·5266	1·5315
	γ-index	1·5258	1·5263	1·5291	1·5320	1·5355	1·5406

The mean refractive index of all these values is 1·5256; and the β-index, corrected for vacuum in terms of the wave-length λ, is $1·5094+511719\lambda^{-2}-894520\times10^{6}\lambda^{-4}$. For the α-index use 1·5072 in place of 1·5094, and for the γ-index use 1·5194 in place of 1·5094. All the indices diminish with a rise of temp., but not equally, for the β-index moves relatively nearer to the γ-index. There is also a diminution in the total amount of the double refraction such that $\gamma-\alpha$ for Na-light decreases from 0·0121 at 15°, to 0·0113 at 80°. The **specific refraction** by H. A. Lorenz and L. Lorentz's formula for the three morphological axes *a*, *b*, and *c* are respectively 0·1748, 0·1721, and 0·1715 for the *C*-line, and for the *G*-line, 0·1787, 0·1759, and 0·1753; the corresponding **specific dispersions** are respectively 0·0039, 0·0038, and 0·0038; and the **molecular dispersions** 0·52, 0·49, and 0·49. The **molecular refractions** by J. H. Gladstone and Dale's formula for the *C*-line are respectively 39·60, 38·87, and 38·70—mean, 39·06. E. Doumer gives 0·325 for the refraction of dil. soln., and 42·9 for the mol. refraction. C. A. Valson, D. Dijken, and J. H. Gladstone have measured the indices of refraction of normal soln.; and A. E. H. Tutton gave for soln. with 35, 40·35, and 40·64 respectively of sp. gr. 1·2030, 1·2334, and 1·2339 at 20° (water at 4° unity), the mean mol. refractions 39·71, 39·53, and 39·76 respectively. The mean refraction of the salt in aq. soln. is therefore 39·67, that is, 0·61 more than for the crystals themselves. O. Pulvermacher made some measurements of the refractive index of aq. soln. W. H. Perkin found the mol. **magnetic rotatory power** for a 40 per cent. soln. at 18° to be 4·98°.

According to W. Hisinger and J. J. Berzelius,[9] an aq. soln. of ammonium

sulphate is decomposed by electrolysis, hydrogen and ammonia appear at the cathode, and ferric sulphate, and later oxygen, at the iron anode. E. Bourgoin found no free nitrogen is formed. For the formation of persulphates, *vide* ammonium persulphate. The **decomposition potential** of a N-soln. with platinum electrodes is found by M. le Blanc to be 2·11 volts—*i.e.* about 0·1 volt less than that of the potassium or sodium salts. Measurements of the **electrical conductivity,** λ, of aq. soln. of ammonium sulphate have been made by F. Kohlrausch, E. Klein, S. Arrhenius, J. H. Long, R. Lenz, S. M. Johnston, etc. For soln. with a mol. of the salt in v litres of water. H. C. Jones and E. Mackay found at 25°:

v	0·8751	3·50	17·50	87·51	350·0	175·0
λ	124·7	161·2	198·5	235·3	260·9	275·1

F. Kohlrausch's values for the temp. coeff. of the conductivity of 5, 10, 20, and 30 per cent. soln. at 15° are 0·0215, 0·0203, 0·0193, and 0·0191 repectively. G. Boizard has investigated the conductivity of mixed soln. of ammonium sulphate and dil. sulphuric acid. If λ denotes the conductivity of the soln. λ' that of the solvent, for a one per cent. soln. of ammonium sulphate, the ratio λ/λ' is a minimum 0·964 with 88 per cent. of sulphuric acid, and it rises continuously with an increasing dilution until with 15 per cent. sulphuric acid, the ratio is unity. For soln. with more than 3 per cent. sulphuric acid, the difference in the conductivities is proportional to the conc. of the ammonium sulphate, but with over 2 per cent. of this salt, the change in conductivity is less marked. In 2 per cent. sulphuric acid, a conc. soln. of ammonium sulphate conducts better, and a dil. soln. worse, than the solvent. If less than one per cent. of sulphuric acid the conductivity is always better than that of the solvent. With soln. containing 25 to 95 per cent. of sulphuric acid, the ratio λ/λ' with rising temp. approaches unity, and the soln. containing 0 to 0·6 and 3 to 25 per cent. of acid, the converse change occurs, and with soln. containing between 0·6 and 3 per cent. acid, both actions can be observed. The **degree of ionization** of the salt in aq. soln. has not been determined exactly. The ionization proceeds in stages: $(NH_4)_2SO_4 \rightleftharpoons NH_4SO'_4 + NH^{\cdot}_4$, followed by $NH_4SO'_4 \rightleftharpoons SO''_4 + NH^{\cdot}_4$, and unless the first stage be completed, the calculation cannot easily be made. From the conductivity and f.p. measurements of a normal soln.. S. Arrhenius calculated for the ternary ionization, $(NH_4)_2SO_4 \rightleftharpoons 2NH^{\cdot}_4 + SO''_4$, the value 2·17 for J. H. van't Hoff's factor i; but the result is not probable. H. Köppe calculated $i=2·00$ for the N-soln. from his osmotic measurements. The effect of additions of non-conductors to the soln. was studied by S. Arrhenius. The degree of ionization with a $\frac{1}{10}N$-soln., at 25°, is 0·0185 with methyl alcohol; 0·0249 with ethyl alcohol; 0·0267 with isopropyl alcohol; 0·0212 with ether; and 0·0171 with acetone.

H. C. Debbits noted that the aq. soln. loses ammonia on boiling as it does at ordinary temp., as is shown by leading a stream of purified hydrogen through a conc. soln.; according to A. R. Leeds, the dissociation is also shown by the aq. soln. at 50·5° reacting acid, the vapour alkaline. H. C. Debbits found that the presence of salts in the soln.—potassium and sodium salts as well as calcium and strontium chlorides—increases the quantity of volatilized ammonia. A. Naumann and A. Rücker found the hydrolysis of soln. of ammonium sulphate to be very small at ordinary temp., but on warming, the soln. becomes acid; they calculate the **degree of hydrolysis** at the b.p. of nN-soln. of ammonium sulphate to be:

n	$\frac{1}{40}N$-	$\frac{1}{8}N$-	$\frac{1}{5}N$-	$\frac{1}{4}N$-	$\frac{2}{5}N$-	N-	$2N$-
Hydrolysis . . .	0·588	0·463	0·413	0·398	0·342	0·230	0·191

This is greater than that of the chloride or bromide. In consequence, it is better to titrate ammoniacal soln. with hydrochloric than with sulphuric acid. C. Brück studied the hydrolysis of boiling soln. of ammonium chloride.

A. Vogel,[10] G. J. Mulder, K. von Hauer, A. E. H. Tutton, and M. Alluard have measured the **solubility** of this salt in water. L. C. de Coppet's and F. Guthrie's

values for soln. below 0° have been indicated above; the eutectic is at −19·05° with 38·4 per cent. of the salt. G. J. Mulder's values for the solubility are:

	0°	10°	20°	30°	40°	60°	80°	100°
Per cent. salt .	41·4	42·2	43·0	43·8	44·8	46·8	48·8	50·8

The determinations at the higher temp. are not so reliable on account of the loss of ammonia by hydrolysis; the sat. soln. boils at 108·9°. There is an unstable 39·4 per cent. soln. at −20·4° with ice as the solid phase. The normal sulphate, $(NH_4)_2SO_4$, is the solid phase between 0° and 100°. According to C. M. van Deventer and H. J. van de Stadt, the increase in conc. per degree is 0·07; and the relative increase in conc. per degree is 0·0035. F. Rüdorff has studied the effect of *ammonium chloride, potassium, copper,* or *zinc sulphate* on the solubility of ammonium sulphate; and A. Fock has studied the solubility of mixed crystals of ammonium and potassium sulphates at different temp. H. Giraud says the salt is easily soluble in sat. aq. *ammonia*.

R. Willstätter found that a soln. of ammonium sulphate in 30 per cent. **hydrogen peroxide** furnishes transparent plates and prisms of $(NH_4)_2SO_4.H_2O_2$. The crystals decompose slowly in **air** and smell of ozone, they also decompose rapidly in vacuo. They are fairly stable in closed vessels, and if warmed under reduced press., highly conc. hydrogen peroxide is obtained. Ammonium sulphate, said J. T. Sheard, absorbs moisture from a damp atm. to an unlimited extent, whether it contains free acid or not; and both acid and neutral samples which have absorbed moisture set to a hard cake when dried.

E. F. Anthon found ammonium sulphate to be insoluble in absolute *alcohol*, while alcohol of sp. gr. 0·872 dissolves 0·2 grm. of the salt, and in more dil. alcohol the salt is more soluble. J. J. Pohl obtained an analogous result. J. Traube and O. Neuberg found that with mixtures of alcohol and water, the soln. separates into two layers with certain conc.—*e.g.* with alcohol with a sp. gr. over 0·9530 at 15°—in the lower aq. layer, the mol. ratio of the three components is approximately constant, indicating that a definite compound is probably formed. These soln. have been studied by G. Bodländer, F. A. H. Schreinemakers, and C. A. L. de Bruyn. This phenomenon, layer separation, has also been observed with lithium sulphate in alcohol-water soln. C. E. Linebarger found the solubility in aq. isopropyl alcohol at 20° to be 0·4, 2·0, and 6·7 grms. $(NH_4)_2SO_4$ per 100 grms. of soln. in the presence of 70, 50, and 20 per cent. of C_3H_7OH. W. Erdmann found ammonium sulphate to be insoluble in *acetone*.

On account of the conversion of normal ammonium sulphate into the hydrosulphate by the loss of ammonia, $(NH_4)_2SO_4 = NH_3 + (NH_4)HSO_4$, W. Smith has emphasized the fact that many of the reactions attributed to the normal sulphate really refer to the hydrosulphate. For instance, K. Stammer says that the red-hot sulphate is reduced to the normal sulphite by **carbon monoxide**; W. R. E. Hodgkinson and N. E. Bellairs found that if heated over the m.p., **copper** furnishes ammonia and hydrogen, but if the temp. be below 160°, cupric sulphate, water, and ammonium sulphite are formed. **Nickel** and **cobalt** act similarly, but less hydrogen, and more sulphite are formed. With **silver**, silver sulphate is formed, and silver dissolves more readily in fused ammonium sulphate than in sulphuric acid, on account of the solubility of silver sulphate in the fused ammonium sulphate. **Palladium** gives a double salt palladium ammonium sulphate; E. Soubeiran found that when heated with **potassium chlorate**, ammonium sulphate decomposes with incandescence, forming chlorine, chlorine oxide, nitrogen, and oxygen; and D. Tommasi that when a little ammonium sulphate is added to fused **potassium nitrite** a vigorous reaction occurs attended by a purple flame, and potassium sulphate, ammonia, nitrogen oxide, and possibly nitrogen are formed. According to A. Emmerling, and E. R. Moritz, a hot or cold soln. of potassium nitrite and acetic acid decompose ammonium sulphate liberating free nitrogen. According to G. Lunge and W. Abenius,[11] and A. A. Hayes, **nitrosyl-sulphuric acid, nitric acid,** or

nitrous acid, or **nitric oxide** can be removed from sulphuric acid by heating the acid with ammonium sulphate—nitrogen or nitrous oxide is formed. M Delepine found that if finely-divided **platinum** be heated with sulphuric acid containing ammonium sulphate, nitrogen is given off: $(NH_4)_2SO_4+2H_2SO_4=H_2SO_4+2NH_4HSO_4=3SO_2+6H_2O+N_2$. The weight of the platinum does not change perceptibly, provided enough of the ammonium salt be present. The platinum is said to act by forming a sulphate $4H_2SO_4+Pt=Pt(SO_4)_2+2SO_2+4H_2O$; followed by $3Pt(SO_4)_2+2(NH_4)_2SO_4=2N_2+3Pt+8H_2SO_4$. M. Delépine has also studied the effect of ammonium sulphate on platinum and iridium salts. According to A. B. Prescott, crystals of ammonium sulphate furnish about 10·2 per cent. of chloride when a gram is evaporated to dryness on a water-bath with 4·035 grms. of **hydrochloric acid** with 1·251 grms. of HCl. According to R. J. Kane, **sulphuric, nitric, and hydrochloric acids** convert normal ammonium sulphate in soln. into the hydrosulphate. J. W. Thomas studied the absorption of hydrogen chloride by soln. of ammonium sulphate. Heat is developed by mixing ammonium sulphate soln. with alkali-lye, thus M. Berthelot found with eq. quantities of ammonium sulphate and **potassium hydroxide,** 1·34 Cals. are evolved, and with sodium hydroxide, 1·25 Cals. H. Schulze obtained the pyrosulphate, $(NH_4)_2S_2O_7$, by heating ammonium sulphate with an excess of **sulphur trioxide.** According to H. Rose, powdered ammonium sulphate absorbs sulphur trioxide slowly at ordinary temp., and the product fuses at a slightly elevated temp., and when heated still higher it decomposes. R. Weber found that ammonium sulphate dissolves in an excess of sulphur trioxide, forming the so-called *ammonium octosulphate*, $(NH_4)_2O.8SO_3$, or *ammonium heptasulphato-sulphate*, $(NH_4)_2SO_4.7SO_3$. According to W. Spring, by distilling ammonium sulphate with **phosphorus pentasulphide,** some ammonium thiosulphate and a little polysulphide and trithionate are formed. R. F. Marchand noted that fused ammonium sulphate attacks **glass.** W. Watson found **oxalic acid** is immediately decomposed by fused ammonium hydrosulphate with the evolution of carbon monoxide and dioxide. The precipitation of **albumen** from its aq. soln. by ammonium sulphate has been studied by A. Hensius and E. Kander.

Normal ammonium sulphate is used in preparing ammonia and the ammonium salts; it is used as a fertilizer; it has been used in purifying sulphuric acid from nitrogen oxy-compounds; in the fermentation industries; and in making freezing mixtures.

Ammonium hydrosulphate, $(NH_4)HSO_4$.—This salt is also called *ammonium acid sulphate, ammonium hydrogen sulphate*, or *ammonium bisulphate*. The crystallization of a neutral soln. of ammonium sulphate furnishes the same salt unchanged, but, as shown by H. Lescœur, if the soln. contains sulphuric acid, crystals of **ammonium hydrosulphate,** $(NH_4)HSO_4$, are formed. The hydrosulphate is obtained by dissolving normal ammonium sulphate in hot conc. sulphuric acid, crystals of the hydrosulphate are deposited on cooling. The mixing of soln. of one eq. each in two litres of water was found by M. Berthelot [12] to be attended by the absorption of 0·93 Cal. R. Bach observed a heat absorption of 14 Cals. E. Mitscherlich obtained thin plates belonging to the monoclinic system by treating a soln. of neutral salt with sulphuric acid. The composition corresponded with **triammonium hydrodisulphate,** $(NH_4)_2SO_4.(NH_4)HSO_4$, or $(NH_4)_3H(SO_4)_2$, the crystals were not deliquescent. The crystal constants were measured by J. C. G. de Marignac. H. Schiff repeated E. Mitscherlich's experiments, and obtained only the primary, that is, the hydro-sulphate; S. W. Johnson and R. H. Chittenden also deny the existence of this salt. G. C. A. van Dorp and J. d'Ans have investigated the equilibrium condition in the ternary system, ammonium sulphate, sulphuric acid, and water, at 30°, and found that three solid phases exist in equilibrium with soln. of the components in different conc. The curve, *BE*, Fig. 58, represents soln. in equilibrium with the solid normal sulphate, $(NH_4)_2SO_4$; *EF*, a like curve for the solid, $3(NH_4)_2SO_4.H_2SO_4$, that is, $(NH_4)_3H(SO_4)_2$, **triammonium hydrosulphate;** *FG*, for the solid hydrosulphate, $(NH_4)HSO_4$;

GH, for **ammonium trihydrosulphate,** $(NH_4)H_3(SO_4)_2$; and *HI*, for **ammonium hydropyrosulphate,** $(NH_4)HS_2O_7$. J. Kendall and M. L. Landon found evidence of $(NH_4)_2SO_4.3H_2SO_4$, *m.p.* 48°, and of $(NH_4)_2SO_4.H_2SO_4$, m.p. 146·9°, on the f.p. curve of the constituents.

When distilled water is evaporated on a water-bath heated by a gas flame, the liquid may be contaminated with ammonium sulphate derived from the gas flame. Ammonium hydrosulphate was found by H. F. Link to form deliquescent rhombohedral and scaly crystals which, according to J. C. G. de Marignac,[13] belong to the rhombic system, and have the axial ratios $a : b : c = 0·6128 : 1 : 0·7436$ According to B. Gossner's study of the mixed crystals, ammonium hydrosulphate is isotrimorphous with potassium hydrosulphate. There are mixed crystals of the type of the crystals of $KHSO_4$, of $(NH_4)HSO_4$, and a monoclinic series of mixed crystals. According to H. Schiff, the granular crystalline mass has a sp. gr. 1·787 ; B. Gossner gave 1·815. J. Traube gives 62·1 for the mol. vol. of the hydrosulphate in a 66·67 per cent. soln. E. Jänecke gave 251° for the m.p. and 490° for the b.p. of the hydrosulphate, and 195° for the eutectic temp. with the normal sulphate. The m.p. given by E. Jänecke is probably over 100° too high because, as indicated in connection with the normal sulphate ; many have obtained numbers nearer 146° for the m.p. of the hydrosulphate—*e.g.* W. Smith, R. Reik, R. F. Marchand, I. Langmuir,

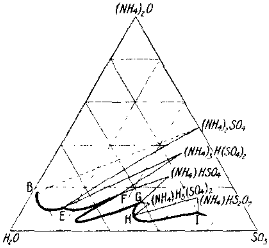

FIG. 58.—Ternary System, $(NH_4)_2SO_4 - H_2SO_4 - H_2O$, at 25°.

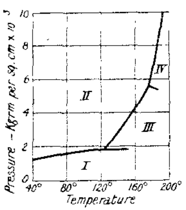

FIG. 59.—Pressure-Temperature Equilibrium Diagram of Ammonium Hydrosulphate.

P. W. Bridgman, etc.—and J. Kendall and M. L. Landon obtained 146·9 ± 0·5°. P. W. Bridgman found that as in the case of potassium hydrosulphate, there are four modifications of the ammonium salt, and very probably yet a fifth form. The temperature-pressure diagram is illustrated in Fig. 59 ; and some data in Table XLIII.

TABLE XLIII.—EFFECT OF PRESSURE ON THE TRANSITION TEMPERATURE OF AMMONIUM HYDROSULPHATE.

Press.		Transition temp.	Change of vol. c.c. per grm.
I–II	1220	40°	0·01330
	1810	120°	0·01188
I–III	1860	130°	0·00529
	1860	150°	0·00529
II–III	2000	128·4°	0·00635
	5000	169·3°	0·00569
III–IV	5650	177·0°	0·00168
	5530	181·0°	0·00265
IV–V	6000	187·3°	0·00466
	10000	193·8°	0·00300

The triple point I–II–III occurs at 126·2° under a press. of 1860 kgrms. per sq. cm.; and II–III–IV at 176·9° and 5660 kgrms. per sq. cm. press.

W. Smith says that the m.p. of ammonium hydrosulphate is 140°. G. Tammann found the lowering of soln. of 9·30, 51·81, 141·28 grms. of the hydrosulphate in 100 grms. of water at 100°, to be respectively 18·6, 112·6, and 257·5 mm. According to W. H. Perkin, the mol. rotation of a conc. soln. is 3·455. The heat of formation, according to M. Berthelot, with sulphuric acid diluted with an equal volume of water, and a mol. of ammonia in two litres of water is $H_2SO_4+NH_3=(NH_4)HSO_4+13·6$ Cals.; and, according to J. Thomsen, $(NH_3aq.H_2SO_4aq)$, 13·37 Cals., and he also found that the heat of soln. of a mol. of the salt in 10, 200, and 800 mols. of water is −0·81, −0·02, and 0·05 Cals. R. Lenz found for the electrical conductivity of soln.:

Eq. per litre	0·250	0·125	0·0625	0·03125	0·015625
λ $(NH_4)_2SO_4$	22·6	25·0	27·2	29·2	31·2
λ $(NH_4)HSO_4$	65·2	73·7	79·2	87·7	98·1

The salt has an acid and bitter taste; and, according to H. F. Link, dissolves in its own weight of cold water. C. F. Gerhardt says the solubility of the salt in alcohol is very small. W. Eidmann says the salt is insoluble in acetone. H. C. Debitts says that when the aq. soln. is boiled very little ammonia is lost. Some of the reactions indicated in connection with the normal sulphate are really produced by the hydrosulphate because the former is converted into the latter when heated above 140°. H. Schulze says that the hydrosulphate loses water and some sulphuric acid when heated in a stream of air between 250° and 300°, and ammonium pyrosulphate is formed. W. Smith found that when heated in an atm. of ammonia, or when ammonia is passed into the fused hydrosulphate, the gas acts as a reducing agent: $3(NH_4)HSO_4+NH_3=2NH_3+3SO_2+6H_2O+N_2$. M. Lachaud and C. Lepierre found the fused salt attacks glass, from which it dissolves the alkali; and alkali sulphates are partially volatilized and partially transformed into hydrosulphate when heated with ammonium hydrosulphate. M. Lachaud and C. Lepierre also studied the oxidation and sulphonation of organic compound by ammonium hydrosulphate. A. Hensius studied the precipitation of albumen from its aq. soln. by ammonium hydrosulphate. According to W. Smith, when ammonium sulphate is heated to 270°–300°, in a current of steam, ammonia gas is driven from the salt, and some sulphur dioxide can also be detected in the gases which are evolved. Nitrogen can be detected between 360° and 400°. The probable reaction is stated by W. Smith to be: $3(NH_4)HSO_4=N_2+NH_4HSO_3+5H_2O+2SO_2$.

Double salts of ammonium sulphate with the alkali sulphates.—Normal ammonium sulphate exhibits a strong tendency to form double or complex salts. This is illustrated by the alums, $NH_4R'''(SO_4)_2.12H_2O$, and by the salts of the type $(NH_4)_2SO_4.R''SO_4.6H_2O$, where R'' denotes bivalent atoms of iron, nickel, cobalt, manganese, zinc, cadmium, magnesium, and copper. A. Arfvedson[14] prepared **lithium ammonium sulphate,** $Li(NH_4)SO_4$, in soluble plates which furnished normal lithium sulphate on calcination. L. Troost also obtained monoclinic plates of this salt by evaporating mixed soln. of the component salts. According to A. Scacchi, the axial ratios of the rhombic bipyramids are $a:b:c=1·6795:1:0·9794$. G. Wyrouboff gives 1·204 for the sp. gr. This variety, called the α-modification, is formed from soln. at about 24°, along with a second variety called the β-modification, which also crystallizes in rhombic bipyramids—pseudo-hexagonal—with axial ratios $a:b:c=1·7303:1:1·6679$, and sp. gr. 1·164. If the temp. of crystallization rises above 24°, the formation of the β-crystals is favoured until, finally, this variety is alone obtained. Both varieties have a positive double refraction. According to G. Wyrouboff, there is yet a third unstable γ-variety which is formed by rapidly cooling the pseudo-hexagonal crystals, and whose optical properties are characteristic of monoclinic crystals. The crystals of lithium ammonium sulphate are not isomorphous with those of the potassium salt, but, according to J. W. Retgers,

they are possibly isodimorphous. According to F. A. H. Schreinemakers and D. H. Cocheret, the solubility of the double salt at $-10°$ is 35·25 per cent., and at 70°, 36·18 per cent.

F. A. H. Schreinemakers and D. H. Cocheret have studied the ternary system water, lithium, sulphate, and ammonium sulphate. Four solid phases—*viz.* $(NH_4)_2SO_4$; $LiNH_4SO_4$; Li_2SO_4; and $Li_2SO_4.H_2O$—were observed at 30°. Fig. 60 represents the composition of soln. of these three components. All possible ternary mixtures of these components can be represented by a point in the triangle; binary mixtures by a point on one of the boundary lines of the triangle; and the pure components by a point on the proper apex. The line *ABCDEF* cuts the triangle into two parts. The line *AB* represents a soln. in equilibrium with the solid phase, monohydrated lithium sulphate, $Li_2SO_4.H_2O$; the sector *AGB* represents soln. which separate into this same solid phase until their composition is that represented by a point on the line *AB*. Similarly for the sector *BHC*, and the line *BC* with respect to the solid phase, Li_2SO_4; for the sector *CIE* and the line *CE* with respect to the solid phase, $LiNH_4SO_4$; and for the sector *EJF* and the line *EF* with respect to the solid phase, $(NH_4)_2SO_4$. The point *B* represents a soln. in equilibrium with the two solid phases, $Li_2SO_4.H_2O$ and Li_2SO_4, and the segment *GBH*, a soln. which separates into a soln. of the composition *B*, and the same two solid phases. The point *C* represents a soln. in equilibrium with the two solid phases, Li_2SO_4 and $LiNH_4SO_4$, and the segment *HCI*, soln. which separate into one of the composition *C* and the same two solid phases. Similarly, *E* represents a soln. in equilibrium with the two solid phases, $LiNH_4SO_4$ and $(NH_4)_2SO_4$, and the segment *IEJ*, soln. which separate into the same two solid phases and a soln. of the composition *E*. The area to the left of *ABCEF* represents unsaturated soln. G. C. A. van Dorp says that the representation of the analytical results by an equilateral triangle is not sufficiently exact; and he found additional solid phases: Li_2SO_4; $(NH_4)_2SO_4$; H_2SO_4; 3 : 1 : 4; 2 : 2 : 4; and 1 : 3 : 4. C. Spielrein has also studied the conditions of equilibrium of mixed soln. of lithium and ammonium sulphates.

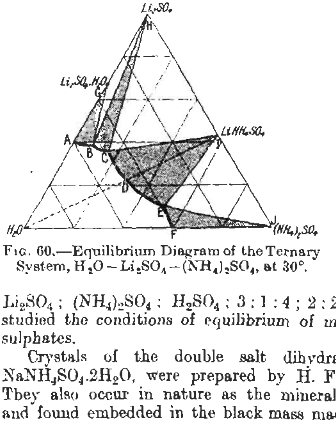

Fig. 60.—Equilibrium Diagram of the Ternary System, $H_2O - Li_2SO_4 - (NH_4)_2SO_4$, at 30°.

Crystals of the double salt dihydrated **sodium ammonium sulphate**, $NaNH_4SO_4.2H_2O$, were prepared by H. F. Link,[15] A. Séguin, A. Riffault, etc. They also occur in nature as the mineral *lecontite*, described by W. J. Taylor, and found embedded in the black mass made up of the excrement of bats in the cave of Las Piedras, Comayagua (Central America). H. Schiff obtained them from a mixed soln. of sodium sulphate and ammonium chloride, or of sodium chloride and ammonium sulphate. The salt was also prepared by E. Mitscherlich from soln. of the mixed components containing an excess of ammonium sulphate, and the crystals are rhombic bipyramids with axial ratios $a:b:c=0·4859:1:0·6630$. The crystals have also been investigated by V. von Lang, and by H. Reinsch. H. Schiff gives 1·63 for the sp. gr. The double refraction is negative. The water of crystallization is lost when the crystals are confined over sulphuric acid, and, according to J. W. Retgers, they can be obtained anhydrous by crystallization over 50°. H. F. Link says that when the crystals are heated, they decrepitate, swell up, give off ammonia and ammonium hydrosulphate, and leave a residue of sodium hydrosulphate. H. Schiff found that 100 parts of water at 15° dissolve 46·6 parts of the hydrated salt, forming a soln. of sp. gr. 1·1749.

According to W. Smith's analyses, the hydrated salt is $Na(NH_4)SO_4.3H_2O$, not $Na(NH_4)SO_4.2H_2O$.

C. Matignon and F. Meyer have studied the ternary system, $H_2O-Na_2SO_4-(NH_4)_2SO_4$, and record the formation of the solid phase, $NaNH_4SO_4.2H_2O$, which is stable in presence of its sat. soln. between 20° and 42°. The heat of soln. is 13·0 Cals. at 15°; and the heat of formation in aq. soln. at 15° is −7·6 Cals. H. M. Dawson has also investigated the system between −20° and +120°, and he found the double salt $Na_2SO_4.(NH_4)_2SO_4.4H_2O$ forms at −16°; the double salt is decomposed by water between −16° and 20°, forming Glauber's salt, and between 41·5° and 59·3° it is decomposed, forming anhydrous sodium sulphate. The transition temp. $Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4+10H_2O$ is depressed to 26·5° by the addition of ammonium sulphate, and at this temp. the system is in equilibrium with three solid phases: the double salt; and anhydrous and decahydrated sodium sulphate. L. Dubrisay studied the temp. of complete miscibility of conc. soln. of ammonium and sodium sulphates. Sodium and ammonium sulphates can be separated by cooling soln. of the appropriate conc.; most of the Glauber's salt separates out, and the ammonium sulphate can be obtained by evaporation at 100°. The separation is not appreciably affected by moderate amounts of free sulphuric acid. These facts have an important bearing on the use of soln. of nitric cake,[16] from the nitric acid works, for the absorption of ammonia in the manufacture of ammonium sulphate.

As indicated previously, mixtures of potassium and ammonium sulphates form a very complete series of mixed crystals, and some members of the series are described in early literature as definite compounds. Thus, H. F. Link[17] and H. Schiff obtained crystals of what was supposed to be the double salt of sp. gr. 2·280, which were said to be stable in air. According to H. Rose, the crystals have $K_2SO_4:(NH_4)_2SO_4$ in the mol. ratio 2 : 1. W. J. Taylor obtained yellowish-white crystals of the composition $5K_2SO_4.(NH_4)_2SO_4$, from the guano beds of the Chincha Islands, and they were called *taylorite* by mineralogists. According to L. R. H. P. Zöller, the composition is variable. The so-called *guanovulite*, found by F. Wibel in guano, and reported to have the composition $K_7(NH_4)_2H_3(SO_4)_6.4H_2O$, is also variable in composition. C. F. Rammelsberg regarded the alleged double salts as mixtures of the component salts.

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§ 28. The Occurrence and Preparation of the Alkali Carbonates

Sodium carbonate is fairly widely dispersed in nature, for it occurs associated with other salts in many mineral waters—*e.g.* Aix-la-Chapelle, Carlsbad, Vichy, etc.—in natron lakes—*e.g.* those of the St. Macarius desert, Egypt; Magadi, British East Africa; near Szegedin (Hungary); Central Africa; the Araxes plain in Armenia; in the plains of Nevada and South California; Mexico; Venezuela (South America); Persia; Tartary; Mongolia; and China—and as dry deposits, efflorescences, or crusts on the ground as *atrun*, *natron*, *trona*, or *urao* in the neighbourhood of the natron lakes and in other places—*e.g.* nearly every district in India; the alkali deserts of Tibet; Utah; and near Lake Texcoco (Mexico). H. Ritthausen,[1] F. Kuhlmann, and A. Vogel found efflorescences which were highly charged with decahydrated sodium carbonate on the walls of certain buildings.

The oldest known deposits of natural soda are those in lower Egypt. They have been described by J. P. J. d'Arcet, X. Landerer, J. Russegger, and E. Sickenberger. There are nine shallow lakes in the Nile valley near Memphis. The waters of some are coloured red. A. Payen ascribes the coloration to the presence of small crustaceæ. The smaller lakes dry up in summer, and the larger lakes leave crusts of salt mixed with clay mud. The crusts are collected, dried, and sold as *latroni*, in the Levant and Greece. It is used in Crete for soap-making. E. Sickenberger says there are 16 lakes in the soda valley—Wady Atrun. Some of these furnish good soda—60 per cent. Na_2CO_3 and upwards—which is called trona, natron, or atrun. T. M. Chatard has shown that it is a mixture of urao with other salts O. Popp and T. Remy have analyzed the salt. There are islands of solid trona in the natron lakes in the oases of Fezzan in the Sahara. M. H. Klaproth, and J. Joffre, have published analyses of this product. The deposit of natural soda at Lake Magadi in the British East African Protectorate covers 30 sq. miles; and amounts to 200 million tons. A. G. Salamon's analysis is:

Na_2CO_3	$NaHCO_3$	$NaCl$	SiO_2	$Al_2O_3+Fe_2O_3$	Water
43·55	40·41	0·36	0·07	0·04	15·57

The Hungarian soda has been known from the time of the Roman dominion as a product of the efflorescence of the soil. The crude soda or *szekso* is collected by scraping, and sold to the refiners, who lixiviate it with water; evaporate the soln. to dryness; and fuse the mass. When cold, the product is broken up and marketed. It is used locally at Szegedin in the manufacture of soap. J. Moser has published an analysis of the raw material, and S. Schapringer, two analyses of the Hungarian soda. The former's analysis is:

Na_2O	K_2O	CaO	Al_2O_3 and Fe_2O_3	SO_3	SiO_2	H_2O	CO_2
8·03	3·12	2·72	2·33	3·48	1·04	15·50	8·79

with a trace of magnesia, and 54·99 per cent. of matters insoluble in nitric acid. E. Kayser, A. Werner, and J. Szabo have also reported on the Hungarian deposits.

H. Abich has investigated the natron lakes of Armenia. The crusts which form about these lakes have from 16 to 23 per cent. of sodium carbonate; 16 to 80 per cent. of sodium sulphate; 2 to 51 per cent. of sodium chloride; and up to about 10 per cent. of water. The mud of Lake Looner (Nizzam, India) dries in summer, and contains a white salt used for washing and soap-making. Wallace's analyses make the soluble portion (74·65 per cent.):

Na_2CO_3	Excess CO_2	K_2CO_3	$NaCl$	$MgCl_2$	Al_2O and $Ca_3(PO_4)$
65·26	7·35	0·27	0·60	0·67	0·50

with a trace of calcium sulphate. According to D. Hooper, saline soils known as *dhobies' earth* occur in numerous places in India, and it has been used for washing, dyeing, glass and soap-making from very early times. The salt is sold in bazaars as *sajji-mati*, and it often contains more sulphate and chloride than carbonate.

R. Haines has analyzed the alkaline deposit—called *duka*, *hurku*, or *kara*—found near Aden in Arabia; it contains 51·05 per cent. Na_2CO_3; 24·94 NaCl; traces of magnesium chloride and sodium sulphate; 19·66 water and organic matter; and 4·35 of sand. It is used for adding strength to snuff, and for washing.

P. Faxar says that the salt urao crystallizes on the bottom of the lake in the valley La Lagunilla in Venezuela, and that it is collected by the natives every two years, and used in the manufacture of *mo*—a dried extract of tobacco used by the natives as a stimulant. J. B. J. D. Boussingault says this urao "crystallizes in prismatic needles arranged in radiating masses; it is a little softer than calcite; the taste is alkaline; and it does not effloresce." His analysis is CO_2, 39·00 per cent.; Na_2O, 41·22; H_2O, 18·80; and impurities, 0·98 per cent. He thus reports on the peculiar way in which the natives obtain the salt:

To collect the urao, the Indians make an excavation on the bottom of the lake, several metres in extent, and plant therein a stake 14 to 16 feet long, the upper end of which reaches above the surface of the water. When this is accomplished an Indian, resting upon this stake, places the end of a second one upon the deposit and holds it at a certain inclination. As soon as this is done, a second Indian glides down the inclined stake, plunges beneath the surface of the water and after a lapse of a few minutes returns with a portion of the salt.

H. F. Keller has described some of the lakes in the valley of Mexico which leave a crust—called *tequezquite*, *confitello*, *tepalcate*, and *espumilla*—consisting of sodium carbonate with sodium chloride, a little nitrate, gypsum, sand, and earthy matter. The product is purified by crystallization to furnish soda crystals—called *sosa bruta*. In the south of Tezcaco, the country people use tequezquite directly without any purification. P. Bénard washed out the sodium chloride with a dil. soln. of the same salt at −18° to −20°, for at this temp. sodium carbonate is virtually insoluble in a sat. soln. of sodium chloride.

The deposits of alkali carbonates in the United States have been described by T. M. Chatard in a memoir: *Natural Soda: its occurrence and utilization* (Washington, 1890). Deposits of alkaline carbonates from alkaline lakes are very common in the Lahontan basin of Nevada and southern California. They form *playas* or *playa lakes* which are dry in summer, and flooded to the depth of a few inches in the wet season. The deposits in Wyoming are said to be typical sulphate deposits resembling those of Armenia; and although they contain more or less carbonate, it is not possible to extract the carbonate economically by natural crystallization. The two soda lakes at Ragtown, Nevada, have been described by F. P. King and by I. C. Russell, and they have been worked for commercial purposes. The deposits have 44 to 52 per cent. of sodium carbonate; 25 to 34 per cent. of sodium bicarbonate; 1 to 5 per cent. of sodium sulphate; 16·3 per cent. of sodium chloride; 14–16 per cent. of water; and 0·2 to 3 per cent. of silica or insoluble matters. Crystals of gaylussacite, $CaCO_3.Na_2CO_3.5H_2O$, are also found in the deposits, although no appreciable amount of calcium appears in the water. This is taken to show that the minute quantities of calcium, which enter the lakes from spring water or otherwise, are immediately removed as gaylussacite. The waters of Mono Lake (California) and of Albert Lake (Oregon) also have a future prospective for profitable working if proper facilities for transport were available. The analysis of the dry residue from the lake water is indicated in Table XLIV. I. C. Russell's analyses of the soluble matters in the waters of Soap Lake (Douglas County, Washington State) and of Owens Lake (Inyo County, California) are included in Table XLIV.

The water of Owens Lake is similar to that of the Albert and Mono Lakes, and it is one of the largest, and most important, sources of natural soda. It is estimated that the lake contains from 20 to 40 million tons of sodium carbonate which is easily obtained of a high degree of purity by solar evaporation in shallow pans. The first crop of crystals was shown by T. M. Chatard to be largely the salt called urao, $Na_2CO_3.NaHCO_3.2H_2O$; the next product in a great part consists of sulphates and chlorides; the mother liquid requires artificial heat for further

evaporation; it is rich in carbonate, and contains the major portion of the potash and boric acid. The manufacture of sodium carbonate on a commercial scale from these waters was begun towards the beginning of 1886. The American market, at least, may be supplied with sodium carbonate from these sources in the near future. S. Poutet, and A. Werner have studied the purification of natural soda by recrystallization from aq. soln.

TABLE XLIV.—ANALYSES OF DRY RESIDUES IN SALINE LAKES.

	Mono Lake.	Albert Lake.	Soap Lake.	Owens Lake.
Dry residue	5·35	3·19	2·82	7·70
SiO_2	0·13	0·59	0·40	0.28
Al_2O_3; Fe_2O_3	0·005	—	—	0·05
$CaCO_3$	0·09	—	—	0·08 ($CaCO_3$ and $MgCO_3$ together)
$MgCO_3$	0·36	—	0·14	
$Na_2B_4O_7$	0·39	—	—	0·63
KCl	3·44	2·62	—	4·07
NaCl	34·60	54·58	20·61	38·16
Na_2SO_4	18·45	2·68	22·89	14·38
Na_2CO_3	34·33	27·09	39·82	34·95
$NaHCO_3$	8·20	12·44	16·14	7·40

The origin of natural soda.—Closed waters must represent a conc. soln. of the water from inflowing streams. Consequently, if a lake contains a given salt, the saline matters must have been brought as such into the basin, or be the result of chemical reactions with other constituents of the lake water. Further, if a salt has been carried into a lake, it must have been leached from the rocks or soils of the region, no matter whether the waters were derived from deep-seated springs or from surface drainage. The origin of the sodium carbonate has been explained by three hypotheses: (1) Percolating water, charged with atm. or volcanic carbon dioxide, has extracted soluble matters from the volcanic rocks, and these have accumulated mainly in the waters of the basin. According to T. M. Chatard, the predominance of sodium salts over potassium salts in natural waters arises partly from the soda rocks being more easily decomposable than potassium rocks, and partly from the fact that on filtration through the soil, potassium salts are retained by the soil to a greater extent than sodium salts. (2) The reduction of alkali sulphates—*e.g.* E. Sickenberger [2] found algæ in the waters of certain natron lakes in Egypt, and noted the evolution of hydrogen sulphide and the deposition of iron sulphide; hence, he suggests that the carbonates were formed by the reduction of sulphates by organic matter, and the subsequent absorption of carbon dioxide from the air. G. Schweinfurth and L. Lewin say that such a process can account for but a small part of the alkali carbonates. H. Abich ascribed the formation of the alkali soils in Armenia to the action of vegetation on the sodium chloride of the soil, which, during the decomposition of the vegetable matter, causes the carbonate to pass into the soil. (3) Double decomposition between calcium bicarbonate and sodium sulphate whereby gypsum is deposited, and sodium bicarbonate or carbonate remains in soln. T. S. Hunt suggested this hypothesis in 1859, and E. von Kvassay used it to explain the formation of the Hungarian deposits when sodium chloride is substituted for the sulphate. C. L. Berthollet, in 1799, and G. Schweinfurth and L. Lewin, in 1898, used the hypothesis to explain the origin of sodium carbonate in the Egyptian natron lakes. Both E. W. Hilgard and S. Tanatar have shown that sodium chloride and sulphate can each react in soln. with calcium bicarbonate to form sodium carbonate. S. Clöez suggests that magnesium bicarbonate is the principal agent in the formation of native sodium carbonate from sodium chloride, but he offers no suggestion as to what becomes of the magnesium chloride.

Efflorescences or crusts are formed either by the partial or complete drying up of the lakes or ponds during summer, or else by the surface evaporation of subsoil moisture carried to the surface by capillary action.

The soda in plant ashes.—Most plants contain the two alkalies—potassium and sodium carbonates—and the former is the dominant constituent in the ashes of most plants, but there are certain species in which sodium carbonate prevails. These plants are found near salt springs, salt steppes, and especially near the sea-shore. Up to the beginning of the nineteenth century, the soda of commerce was made from the ashes of sea plants and from trona. The ashes of seaweeds, remarkably enough, contain very little alkali carbonate, and the potash usually predominates. The potash in the ashes of seaweeds ranges from 4 to 24 per cent. and the soda from 2 to 24 per cent. It is probable that the soda plants in the vicinity of the sea convert sodium chloride into sodium oxalate, tartrate, etc., which, on being incinerated, yield the carbonate. The more important soda plants are the atriplex portulacoides, tragus, and kali; many species of the chenopodium; salsola soda, kali, tragus, arenaria, clavifolia, vermiculata, and branchiata; salicornia annua, arenaria, and europœa; cochia sedoides; statice limonium; triglochin maritimum; several fidoideæ—reaumeria, tetragonia, nitraria, and mesembryanthemum. According to T. Richardson and W. Watts,[3] the ashes of the following plants gave the percentage yield of sodium carbonate:

Salsola clavifolia.	Salsola soda.	Halmiocicimum capsicum.	Salsola kali.	Kochia sedoides.	Salsola brachiata.
45·99	40·95	36·75	34·00	30·84	26·26

The dried plants were incinerated in pits or in special furnaces. The product made in pits varied in colour and texture with the treatment, and some varieties made in the same place and apparently in the same way received special names—thus, *soude douce* was a well-fluxed ash-like mass with 20 to 25 per cent. of sodium carbonate; *soude mélangée*, a dark-coloured honey-combed mass with a sharp fracture: and *soude bourde*, a low quality mixed with particles of coke, and contained much common salt and earthy matters. The Spanish soda enjoyed the best reputation, and its special name *barilla* has been genetically used for soda made from plants. Two derivations have been suggested for the word *barilla*—also spelt *barrilla*. In one, the term is supposed to be a corruption of the Spanish *barril*—cask or barrel; and in the other, the term is derived from the Spanish *barrilla* or *varrilla* applied to the plants which are grown for making barilla. Vegetable soda or barilla is the more or less fluxed ash from incinerated plant, which has not been purified by lixiviation, and which contains all the inorganic constituents of the plants. J. P. L. Girardin has analyzed a number of varieties of barilla. In these analyses there was up to about 3 per cent. of insoluble matter, and the soluble matter included the two alkali carbonates, sulphates, and chlorides with a small proportion of sulphide and thiosulphate. *Alicante soda*, *Cartagena soda*, and *Malaga soda* were trade names for varieties of Spanish soda; *salicor* or *soude de Narbonne* was made from the salicornia annua, and it has 14 or 15 per cent. of sodium carbonate; *blanquette* or *soude d'Argues-mortes* was obtained from varieties of the atriplex—portulacoides, tragus, or kali-salicornia europœa, and the statice lemonium—and had 4 to 10 per cent. of sodium carbonate. The soda from Teneriffe was derived from the mesembryanthemum crystallium, and had about 20 per cent. of sodium carbonate. Some low-grade soda was also made from varec in the North of France—*sel de varec*—and from Scotch and Irish kelp.

The preparation of sodium and potassium carbonates.—According to N. N. Beketoff,[4] sodium oxide, Na_2O, is not attacked by carbon dioxide at ordinary temp., but at 400° the two substances unite suddenly and vigorously with incandescence. Carbon dioxide transforms the moist oxide or hydroxide into carbonate. The low solubility of sodium hydrocarbonate enables it to be prepared in a very fair degree of purity, and it is quantitatively converted into equally pure carbonate by

ignition in a weighed platinum crucible at a dull red heat for 10–15 min. The salt should not be allowed to fuse. It is cooled in a desiccator and weighed; 84 grms. of hydrocarbonate should give 53 grms. of the normal salt. To ensure that decomposition, $2NaHCO_3=Na_2CO_3+H_2O+CO_2$, is complete, the crucible is again heated another 10 min., and again weighed. According to H. Kunz-Krause and R. Richter,[5] the change occurs at 250° if the mass in the crucible be stirred with a platinum wire so that all portions are brought into contact with air. According to P. Melikoff and M. Rozenblatt, when ammonium carbonate is added gradually to fused sodium or potassium chloride in a platinum crucible, sodium or potassium carbonate is formed in amount depending on the quantity of ammonium carbonate added. The reaction: $2NaCl+(NH_4)_2CO_3\rightleftharpoons Na_2CO_3+2NH_4Cl$, is reversible. If ammonium carbonate and chloride are added together to the fused sodium chloride, no sodium carbonate is formed. If sodium or potassium sulphate be similarly treated, the corresponding carbonate is not formed.

The preparation of sodium carbonate from impure natural soda, and from the ashes of soda plants, has been already described. Methods have also been suggested for transforming various sodium salts—sulphate, chloride, fluoride, cryolite, nitrate, and felspar—into the carbonate. Many of these are discussed in detail by R. von Wagner's *Regesten der Sodafabrik* (Leipzig, 1866); and by G. Lunge's *A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali* (London, 1896). Much of what is said of the sodium salts applies also to the potassium salts, and conversely.

The preparation of potassium carbonate from potassium salts of the organic acids.—The preparation of potassium salts from kelp ashes, wood ashes, vinasse, suint, alumino-silicate minerals—*e.g.* felspars, zeolites, prophyries, syenites, trachytes, etc.—has been described. It was formerly the custom to prepare a purer form of potassium carbonate by the ignition of cream of tartar, potassium hydrogen tartrate. This salt was heated in a covered iron crucible, and the mixture of carbon and potassium carbonate was lixiviated with water, and the soln. evaporated in a silver basin. The product was hence called *salt of tartar*, or *sal tartari*, or *kali carbonicum e tartaro.* According to H. W. F. Wackenroder,[6] the product contains traces of chlorides, calcium and magnesium salts, and potassium cyanide if crude cream of tartar be used, and, according to A. Vogel, potassium phosphate. Hence, it has been recommended to purify the cream of tartar by digesting it for an hour with its own weight of water and $\frac{1}{16}$th of hydrochloric acid; the undissolved cream of tartar is washed until free from calcium salts. If a clay crucible be used for the incineration, the product will contain some silica; but H. W. F. Wackenroder says this can be avoided by lining the crucible with a mixture of starch and gum. J. S. Stas purified the cream of tartar used in his work on at. wt. by digesting it with 5 per cent. hydrochloric acid, washing and drying in order to make the silica insoluble. Then he recrystallized the cream of tartar, and incinerated the product in a silver crucible to get potassium carbonate. G. C. Wittstein, A. Gatty, R. von Wagner, N. Gräger, and N. Bloch have discussed the purification of cream of tartar for use in this process of making potassium carbonate. Potassium carbonate has been prepared by calcining potassium acetate, $CH_3.COOK$; and U. Duflos used potassium acid oxalate. Carbon dioxide has also been passed into an alcoholic soln. of potassium acetate. This furnishes a mixture of potassium carbonate and bicarbonate which can be afterwards calcined for the carbonate.

The preparation of sodium carbonate from sodium fluoride.—M. Krantz treated a soln. of sodium fluoride with gelatinous silica and carbon dioxide when two-thirds of the sodium fluoride is converted into sodium bicarbonate, and one-third into sodium fluosilicate: $6NaF+SiO_2+4CO_2+2H_2O=4NaHCO_3+Na_2SiF_6$. The sodium fluosilicate is converted back to sodium fluoride by treating it with a slip of powdered fluorspar: $Na_2SiF_6+CaF_2=CaSiF_6+2NaF$. W. Weldon patented a complicated process in 1866, which has not been practically applied. W. Weldon treated sodium sulphate with hydrofluoric acid: $Na_2SO_4+HF=NaHSO_4+NaF$, when

sodium fluoride is alone precipitated; this can be decomposed by magnesia: $2NaF+MgO+H_2O=2NaOH+MgF_2$; the magnesium fluoride is converted into sulphate with the recovery of the hydrogen fluoride by heating it with the sodium bisulphate previously formed: $2MgF_2+2NaHSO_4=2MgSO_4+2NaF+2HF$: and the magnesium sulphate when treated with sodium chloride forms sodium sulphate which crystallizes out at —4°, and a soln. of magnesium chloride is obtained. On ignition with steam magnesium chloride forms magnesium oxide and hydrochloric acid. F. Jean (1868) devised a process for sodium fluoride by heating the sulphate, with coal, fluorspar, and calcium carbonate. The reaction is said to be very incomplete.

The preparation of sodium carbonate from cryolite.—Cryolite, sodium fluoaluminate, Na_3AlF_6, can be worked up into sodium carbonate and alumina by a process devised by J. Thomsen[7] in 1862. An intimate mixture of equal weights of finely ground cryolite and calcium carbonate is heated to dull redness. The calcined residue is called *cryolite ash*. During the calcination, calcium fluoride and sodium aluminate are formed, while carbon dioxide is set free: $Na_3AlF_6+3CaCO_3=Na_3AlO_3+3CaF_2+3CO_2$. The action is more complete if a little calcium fluoride from a previous operation is incorporated with the initial mixture. The charge from the furnace while hot is discharged into water contained in wooden lixiviating vats with false bottoms. Sodium aluminate dissolves, and the soln. is pumped into boilers to be treated with carbon dioxide. The insoluble residue—mainly calcium fluoride—is employed in making glass, enamels, and bricks, and as a flux for metallurgical purposes. Carbon dioxide is forced into the soln. of sodium aluminate when aluminium hydroxide is precipitated, and sodium carbonate remains in soln.: $2Na_3AlO_3+3CO_2+3H_2O=2Al(OH)_3+3Na_2CO_3$. A comparatively large proportion of the sodium carbonate is absorbed by the precipitate, and requires much washing with boiling water. The alumina is mainly used for making alum. The soln. of sodium carbonate is conc. to a sp. gr. 1·332, when sal soda, $Na_2CO_3.10H_2O$, crystallizes out; the lye can also be converted into the hydrocarbonate $NaHCO_3$, by the action of carbon dioxide.

F. G. Spilsbury patented J. Thomsen's process in 1856; C. Tissier could only decompose one-third the cryolite in this way, and D. Sauerwein showed that for complete decomposition, 336 parts of calcium carbonate are needed for 447 parts of cryolite. H. Schwarz, J. Bing and J. L. Smith have described J. Thomsen's cryolite process. J. R. von Wagner suggested baryta in place of lime. L. Schuch proposed decomposing cryolite with boiling soda-lye; H. Bauer with a mixture of calcium carbonate and soda-lye; F. Lauterborn suggested boiling the cryolite with water alone; and J. F. Persoz, by the treatment with sulphuric acid: $2Na_3AlF_6+6H_2SO_4=Al_2(SO_4)_3+3Na_2SO_4+12HF$. The difficulty in separating the sodium and aluminium sulphates rendered the process of no use industrially.

The preparation of alkali carbonate from the alkali chlorides.—T. Bergmann[8] (1775) showed that a soln. of sodium chloride is decomposed by potassium carbonate, for the mixed soln. on evaporation gives a crop of crystals of potassium chloride, and this is followed by a crop of crystals of sodium carbonate. J. F. Meyer (1764), and J. F. Westrumb (1785) gave specific directions for the operation, and the same plan was recommended by C. F. S. Hahnemann, P. J. Karstellyn, and J. C. W. Remler. Between 1802 and 1815 sodium carbonate was made at Walker-on-Tyne by a modification of the process devised by Earl of Dundonald (1795). C. Bischoff made sodium bicarbonate by passing carbon dioxide into an aq. soln. of equal parts of sodium chloride and potassium carbonate—sodium bicarbonate precipitated, potassium chloride remains in soln. W. Weldon patented a modification of this process in 1881.

C. W. Scheele (1773) noted that a damp mixture of common salt and calcium hydroxide effloresces after some weeks' exposure to air, the efflorescent salt is sodium carbonate. It is probable that calcium bicarbonate is formed, which precipitates soluble sodium bicarbonate, and this explains the formation of the efflorescence of soda from salty soils. The observation made by C. W. Scheele

was also made, perhaps independently, by J. L. Proust, B. Pelletier, and N. Deyeux, and was the subject of a patent by M. Carny in 1792, and worked for some time at Crosie. C. W. Scheele (1773) also noted that a soln. of common salt is decomposed by litharge, for, when the salt soln. is filtered through the lead oxide, it becomes caustic, and in air it yields sodium carbonate. T. Bergmann described C. W. Scheele's observation in 1775. The insoluble by-product of the reaction is yellow lead oxychloride: $2NaCl+2PbO+H_2O=2NaOH+ClPb.O.PbCl$, and the preparation of this compound was patented by J. Turner in 1781, and it was employed as a pigment under the name *Turner's yellow*—sodium hydroxide was then a by-product. F. C. Achard (1784) did not favour the process. Many patents have been based on C. W. Scheele's reaction—*e.g.* F. R. Curaudau (1792), C. Watt and T. R. Tebbutt (1838), J. Hunt (1839), J. Rowbotham (1866), F. M. Bachet (1869), D. C. Knab (1877), Société anonyme Lorraine industrielle (1882), and F. T. Romiquières (1888). Zinc oxide is not so good as lead oxide for the purpose.

The preparation of sodium carbonate by the action of ammonium carbonate on sodium chloride is treated in a special section on the Solvay process. G. Tauber proposed to use ammonium sulphite in a similar manner: $4NaCl+4(NH_4)_2SO_3=2Na_2(NH_4)_2(SO_3)_2+4NH_4Cl$. The precipitated double salt is separated by the centrifuge and heated to 100°, whereby normal sodium sulphite remains as a residue, and ammonia, sulphur dioxide, and steam are evolved as vapours. The sodium sulphite is decomposed by lime with calcium sulphite as a by-product. W. Weldon exposed a mixture of water, common salt, and magnesia or magnesium carbonate to the action of carbon dioxide under press., when sodium bicarbonate is precipitated: $2NaCl+MgCO_3+CO_2+H_2O=2NaHCO_3+MgCl_2$. The method has not been successful for the manufacture of soda, but C. R. Engel has applied it to the manufacture of potassium carbonate. A. Lanquetin substituted dolomite in place of W. Weldon's magnesium oxide or carbonate; and E. Carthaus, recommended a little ammonium salt to prevent the precipitation of basic salts. A number of patents have been taken for converting sodium chloride into carbonate by the action of carbon dioxide with carbon monoxide or hydrogen on heated sodium chloride alone or admixed with carbon or a metal—*e.g.* R. Lancaster (1879), M. Benze and F. von Hardtmuth (1893), G. Duryee (1880).

The potassium carbonate manufactured from the Stassfurt salts is in a great measure made by Engel's process, which depends on the fact that below 24° potassium chloride in the presence of magnesium carbonate is decomposed by carbon dioxide, forming an almost insoluble double salt, $KHCO_3.MgCO_3.4H_2O$, and magnesium chloride: $3MgCO_3+2KCl+CO_2+5H_2O=MgCl_2+2MgKH(CO_3)_2.4H_2O$. The sparingly soluble double salt is readily separated from the soln. of magnesium chloride, washed, and either heated with warm water: $2MgKH(CO_3)_2.4H_2O=2MgCO_3+K_2CO_3+CO_2+5H_2O$, or treated with magnesium hydroxide below 20°. The soln. of potassium carbonate is filtered off; the magnesium carbonate and carbon dioxide are used for the treatment of more potassium chloride. The decomposition proceeds better under half an atm. press., and at a temp. over 115°, since the magnesium carbonate is then in a form which filters easily, and the formation of bicarbonates is avoided.

Patented proposals have been made to heat sodium chloride with phosphoric acid (A. Delhaye); zinc or lead pyrophosphate (L. J. F. Margueritte); or ferric phosphate (A. R. Arrott). The resulting soluble sodium phosphate is decomposed by boiling with lime to form sodium hydroxide, which, if needed, can be converted into carbonate by a current of carbon dioxide. These methods are quite impracticable. In 1809, J. L. Gay Lussac and L. J. Thénard proposed to make soda by the action of steam on a mixture of sodium chloride and silica: "If these two compounds are melted together there is very little action, for the salt volatilizes before anything but a superficial combination takes place, and the action of salt in the glazing of pottery is probably made possible by the aq. vapour in the furnace gases." The sodium silicate formed by the joint action of sodium and

steam on silica is suspended in water and treated with carbon dioxide, whereby sodium carbonate and gelatinous silica are formed. The process was the subject of patents by A. Blanc and T. P. Bazille (1840), G. Fritsche (1858), W. Gossage (1862), and T. Williams (1881). In 1848, A. Böhme found that boric acid decomposes sodium chloride in the presence of steam, forming hydrochloric acid and sodium borate; and L. J. F. Margueritte (1855) patented the process, converting the sodium borate by lime into sodium hydroxide and calcium borate, and from the latter the boric acid is recovered by, say, treatment with hydrochloric acid. W. Garroway (1889) also devised a modification of the process. T. Greenshields (1852) treated a red-hot mixture of gypsum and coal with a mixture of coal and sodium chloride. The lixiviated product was mixed with coal and limestone, fused in a reverberatory furnace, and afterwards leached with water for sodium carbonate. T. Raynaud (1890) heated common salt with ferrous sulphide in air; chlorine was given off, and the mixture of ferric oxide and sodium sulphide so formed was fused with coal. The resulting sodium carbonate and ferrous sulphide were lixiviated with water: the insoluble ferrous sulphide was used over again.

W. Weldon's patent (1866) for decomposing sodium chloride by hydrofluoric acid, boiling the resulting sodium fluoride with magnesium oxide, and decomposing the magnesium fluoride by sulphuric acid, has been indicated in dealing with the sulphates. E. L. M. Brochon makes hydrofluoric acid act on sodium chloride either fused or in soln. According to W. Weldon, sodium chloride can only be partially decomposed by treating a sat. soln. with hydrofluoric acid, but a moderately quick current of the gas is passed into a soln. of sodium chloride. F. G. Spilsbury and W. Maugham (1837) mixed a soln. of sodium chloride with hydrofluoric acid, or, better, with hydrofluosilicic acid, and converted the precipitated sodium fluosilicate into calcium fluosilicate and sodium hydroxide by boiling it with milk of lime. The washing of the precipitates is very difficult. H. le Chatelier and C. Kessler patented a similar process in 1858.

In 1847, R. A. Tilghmann patented a process for making sodium carbonate by heating a mixture of sodium chloride (or sulphate) and alumina in a current of steam: $Al_2O_3+2NaCl+H_2O=2NaAlO_2+2HCl$. The sodium aluminate is dissolved in hot water and treated with carbon dioxide whereby aluminium hydroxide is precipitated, and a soln. of sodium carbonate is formed. The action is not very energetic at a red heat, and the use of a higher temp. introduces difficulties with the refractories. W. Gossage (1862), J. Hargreaves (1867), and H. Grüneberg and J. Vorster (1874) patented a similar process to that of R. A. Tilghmann. J. Anderson (1867) and A. Kayser (1887–1891) used clay in place of alumina; and R. Lieber (1887) used aluminium sulphate, and, in 1878, a mixture of alumina and magnesium sulphate; M. Swager (1868) used a mixture of sodium and aluminium chlorides. C. Kessler (1867) and I. M. Gattman (1868) heated in a current of superheated steam and air a mixture of sodium (or potassium) chloride with chromic oxide alone or mixed with manganese oxide, chrome iron ore, or lead chromate. Sodium dichromate and hydrogen chloride are formed: $4NaCl+2Cr_2O_3+2H_2O+3O_2=2Na_2Cr_2O_7+4HCl$. A mixture of the solid product of the reaction with coal is heated to dark redness, when a mixture of chromic oxide and sodium carbonate is formed: $Na_2Cr_2O_7+2C=Na_2CO_3+Cr_2O_3+CO$; and $2Na_2Cr_2O_7+3C=2Na_2CO_3+2Cr_2O_3+CO_2$. The latter is removed by lixiviation with water; the insoluble chromic oxide can be used again. The reaction between steam and the mixture of sodium chloride and chromic oxide is very incomplete. J. Hargreaves and T. Robinson reduced with hydrogen, carbon monoxide, or the hydrocarbons, forming in the first case sodium hydroxide, and in the other two cases sodium carbonate.

A. Vogel has shown that sodium chloride can be converted into the oxalate by treatment with oxalic acid; and on ignition, sodium carbonate is formed. When sodium oxalate is boiled with calcium oxide, calcium oxalate and sodium hydroxide are produced. Processes founded on these reactions were patented by E. Samuel (1838), L. J. F. Margueritte (1855), and W. Weldon (1866). G. Bong (1875) used

ammonium oxalate in place of oxalic acid; E. Bohlig recommended magnesium oxalate. According to F. W. Dupré,[9] if a soln. of potassium sulphate and sodium carbonate sat. at 0°, be cooled to −6°, crystals of sodium sulphate, Glauber's salt, separate. The same soln. can be again sat. with potassium sulphate and sodium carbonate, and the process repeated until the soln. is sufficiently enriched with potassium carbonate. F. W. Dupré also says that in this process better results are obtained if potassium sodium sulphate is obtained from a mixture of sylvinite and Glauber's salt at 1½–8 atm. press.

The preparation of alkali carbonate from alkali sulphate.—In 1786, J. F. Hagen described the double decomposition between sodium sulphate and potassium carbonate in aq. soln., when the less soluble potassium sulphate crystallized out first, and crystals of sodium carbonate were obtained from the mother liquid. According to F. C. Accum, this process was used in London prior to 1808. The same process has been described by T. Bergmann, J. F. Westrumb, and J. F. W. Nasse, and if the then ruling prices of potash and soda be taken into consideration, was not so economically absurd as might at first sight appear in the light of our present-day knowledge; indeed, in 1840, E. F. Anthon reported favourably upon his application of the process on a big scale. In another series of processes, the sodium sulphate was converted into the sodium salt of an organic acid, and the latter calcined for the carbonate—thus, L. F. F. von Crell (1778), and C. A. Millet (1812), J. B. Mollerat, and A. Payen, and W. A. Lampadius treated sodium sulphate with calcium acetate; and R. Kirwan (1789) used lead acetate—E. F. Anthon (1842) found that barium acetate, and calcium, lead, or barium sulphate was respectively precipitated, and he evaporated the soln. of sodium acetate to dryness, and roasted the product. F. Frerichs obtained a patent for a similar process in 1890, and proposed to get acetone from the volatile products of the decomposition of the sodium acetate. J. B. M. P. Closson proposed to treat sodium sulphate with calcium saccharate, and he decomposed the resulting soln. of sodium saccharate, by carbon dioxide, into sugar and sodium bicarbonate. W. W. Staveley heated calcium carbonate with cresol or phenol, and sodium sulphate; calcium sulphate was precipitated, and the aq. soln. of sodium phenolate or cresolate was decomposed by carbon dioxide. The Chemische Fabrik Grünau described a similar process using α- and β-naphthols, etc.

The preparation of sodium carbonate by heating sodium sulphate with limestone and coal will be discussed in a special section devoted to N. Leblanc's process. Potassium carbonate is made by the same process. In 1783, H. F. Delius proposed decomposing sodium sulphate by calcium oxide into sodium hydroxide and calcium sulphate. The same process was used by F. C. Achard, C. W. Scheele, and M. H. Klaproth. P. Claussen (1852) patented the use of the hydroxides of barium, strontium, or calcium for a similar purpose, and changed the hydroxide to carbonate by exposure to air. E. F. Anthon (1840) showed that the reaction is incomplete, and accordingly A. G. Hunter (1865) and C. M. T. du Motay (1871) proposed to heat the mixture of lime and sulphate with water under press.; but D. Hill, M. Reisz, and E. T. Bevan and C. F. Cross did not obtain encouraging results. D. Hill found a 1 per cent. conversion without press.; a 6 per cent. conversion with 3 atm. press. M. Fries found the reaction with calcium oxide progressed more completely if a little barium carbonate be present—*vide infra*. The double decomposition is virtually complete if barium hydroxide be substituted for calcium oxide even in cold soln., and this would be an efficient way of making soda if it were possible to make barium oxide cheaply enough; indeed, said A. W. Hofmann, when a much cheaper process for making caustic baryta than any at present known, has been discovered, then the manufacture of alkali will be revolutionized. A patent for the baryta process was obtained by H. P. Fuller in 1819; he made his baryta by calcining the carbonate, and used the carbon dioxide for carbonating the sodium hydroxide. Modifications were proposed by E. Samuel, G. Hofäcker, A. G. Hunter, W. A. Lyttle, and A. Smith; and the

substitution of strontium oxide for calcium or barium oxide has been suggested by A. Ungerer, G. H. Gray, and F. Eichstädt. Several attempts have been made to decompose the sulphate either by fusion with barium (or strontium) carbonate, as was done by C. W. G. Kastner in 1826, and E. F. Anthon in 1840; or by boiling barium (or strontium) carbonate with a soln. of sodium sulphate as proposed by L. W. Kölreuter in 1824. In neither case has the result been successful. The reaction is incomplete because a large proportion of sodium sulphate remains undecomposed, as was demonstrated in 1832. Nevertheless, the reaction has been the subject of many patents—C. Lennig (1851), W. H. Balmain and T. Colby (1856), and M. Nauhardt (1892). H. Rose, and F. J. Malaguti have studied the equilibrium conditions of the reaction; and W. Spring, the effects of press.

J. Townsend patented the use of a mixture of barium carbonate and calcium oxide for converting the sulphate to carbonate. D. Hill and G. Lunge found that the reaction is complete with precipitated barium carbonate, but not with native carbonate, provided an excess of the carbonate and lime be used, the cost also is prohibitive. M. Pongowsky patented the process of converting sodium sulphate into carbonate by adding powdered limestone to an alkaline soln. of the sulphate, and treating the mixture with carbon dioxide with constant agitation. Calcium bicarbonate is formed, and this converts the sodium sulphate into carbonate. E. W. Hilgard verified the conclusion and suggested the reaction as an explanation of the formation of natural soda; but G. Lunge showed that dil. soln. are required, and on evaporation, the reaction is reversed. H. Taylor (1851) used barium bicarbonate under similar conditions; and R. von Wagner showed that a clear soln. of barium bicarbonate decomposes sodium sulphate, forming barium sulphate and sodium bicarbonate, and that a comparatively small proportion of the bicarbonate will complete the reaction between barium carbonate and sodium sulphate. F. Kuhlmann obtained better results by increasing the press. The cost of the process renders the process unable to compete with the ammonia process. Patents have been obtained by G. Lunge (1866), W. Bramley (1886), and W. von Baranoff (1895) for modifications of this process. J. L. Smith prepared potassium carbonate by shaking for an hour a mixture of calcium carbonate with a soln. of potassium sulphate sat. with carbon dioxide. H. Jannasch also patented the preparation of potassium carbonate from kainite by treating potassium sulphate with witherite.

R. A. Tilghmann (1847) and E. Siermann (1878) proposed converting sodium sulphate into carbonate by a process based on this fact, that while a mixture of sodium sulphate and alumina is not decomposed even at a white heat, a reaction occurs if steam be present. Bauxite behaves similarly, while iron oxide acts better if the temp. be very high. Sodium aluminate is formed. The reaction is incomplete, for there is only a 40 per cent. conversion of sodium sulphate into the aluminate. An aq. soln. of the product can be decomposed by carbon dioxide into alumina and sodium carbonate; or, according to G. and F. Löwig, by treatment with milk of lime. C. R. Claus obtained better results with reducing gases; H. M. Baker mixed the alumina with coal; D. A. Peniakoff, with pyrites: J. C. H. Behnke and E. Fleischer used a mixture of sodium sulphate, coal, bauxite, and ferric oxide. The furnace operations involved in these processes severely corrode the refractory linings.

A. Baudrimont and J. Pelouze (1833) fused the sodium sulphate with galena or zinc blende and formed the alkali plumbate or zincate, and J. B. M. P. Closson boiled a soln. of sodium sulphate with milk of lime and lead oxide. The plumbate can be decomposed by sulphide, carbon dioxide, or by electrolysis. The St. Gobain Co. patented a process in which sand, coal, and sodium sulphate are heated together; water-glass is formed; and a soln. or suspension of that salt in water is decomposed by carbon dioxide or by milk of lime. J. Simpson (1890), J. C. Ody (1892), N. Basset and W. von Baranoff (1894) decomposed a soln. of sodium sulphate by calcium phosphate in dil. acid. The soluble sodium phosphate which is formed

when treated with milk of lime. gives a precipitate of calcium phosphate and a soln. of sodium hydroxide. G. E. Davis (1877) used commercial aluminium phosphate in place of the calcium salt. F. Gutzkow decomposed a soln of sodium sulphate with calcium bisulphite; calcium sulphate is precipitated and a soln. of sodium sulphite is formed; the sodium sulphite is decomposed by milk of lime, forming calcium sulphite and sodium hydroxide. J. J. Alsberge proposed an analogous cycle with calcium oxalate and sodium bisulphate. In W. Weldon's and F. Jean's processes, the sulphate (or chloride) is treated with barium sulphide, a soln. of potassium sulphide, and a precipitate of barium sulphate are produced. This reaction was the subject of a patent by the Chemische Fabrik Buckau. The sulphide soln. was evaporated to a sp. gr. of 1·16, and treated with carbon dioxide, which converts the sulphide to carbonate with the evolution of hydrogen sulphide. The potassium carbonate is recovered by evaporation.

P. Römer mixed a hot conc. soln. of equi-molecular parts of potassium sulphate and dichromate with enough milk of lime to precipitate the combined sulphuric acid as calcium sulphate. The precipitate was removed from the soln. of potassium chromate: $Ca(OH)_2+K_2SO_4+K_2Cr_2O_7=2K_2CrO_4+CaSO_4+H_2O$. The soln. was evaporated until it was sat. between 35° and 40°, and treated with carbon dioxide, which converted the chromate to dichromate and hydrocarbonate: $2K_2CrO_4+2CO_2+H_2O=2KHCO_3+K_2Cr_2O_7$. The purification of the soln. of potassium hydrocarbonate was effected by repeated evaporation and saturation with carbon dioxide. The process can also be employed for kainite, schönite, sylvinite, etc.

The preparation of alkali carbonate from alkali sulphide reduced from the sulphate.—According to J. Mactear,[10] the note-books of Tennant's works, dated about 1800, say that sodium carbonate can be made by heating sodium sulphate with coal, and that when the product is lixiviated, evaporated for crystallization, and again calcined, the product becomes richer in carbonate; J. von Liebig made an analogous proposal to the same firm in 1839, and stated that when the calcination is made at 300°, the sodium oxalate and acetate first formed are decomposed into the carbonate. The failure of the process was ascribed by J. von Liebig to the reaction following a different direction to the way he thought it would go, *viz.*, $2Na_2SO_4+4C=Na_2CO_3+Na_2S_2+2CO_2+CO$. W. Gossage (1869) tried to make sodium hydroxide by running melted sodium sulphate through red-hot coke—the sulphur was supposed to be liberated in a free state. In N. Leblanc's process, to be subsequently described, the sodium sulphate is converted into carbonate by heating it with admixtures of coal and calcium carbonate. G. Reinar (1858) proposed to use barium carbonate in place of the calcium carbonate in N. Leblanc's process in countries where native barium carbonate "occurs in large quantities." There are few places where barium carbonate does occur in large quantities; a greater weight of material has to be handled for a given result; and, as R. von Wagner showed, the results are unsatisfactory with a large excess of barium carbonate since sulphide accumulates in the liquors.

In 1778, Père Malherbe ignited sodium sulphate mixed with charcoal and iron in a reverberatory furnace, and lixiviated the cold mass with water to get the sodium carbonate. F. E. Siemens (1828) used a mixture of manganese dioxide and iron for decomposing the sodium sulphide, and E. Kopp (1854) substituted ferric oxide for iron in Père Malherbe's process. According to E. Kopp, the reaction progresses: $2Fe_2O_3+3Na_2SO_4+16C=Na_6Fe_4S_3+14CO+2CO_2$, followed by $Na_6Fe_4S_3+O_2+2CO_2=Na_2Fe_4S_3+2Na_2CO_3$. When the supposed $Na_2Fe_4S_3$ is oxidized in damp air and calcined the end products are $Na_2Fe_4S_3+7O_2=2Fe_2O_3+Na_2SO_4+2SO_2$. On the other hand, A. Stromeyer says the double sulphide arising out of the process is $Na_2S.2FeS$, *i.e.* $Na_2Fe_2S_3$, and not E. Kopp's $Na_6Fe_4S_3$; and he represents the reaction: $2Fe_2O_3+6Na_2SO_4+13C=2Na_2Fe_2S_3+4Na_2CO_3+9CO_2$. A. Stromeyer says E. Kopp's second equation cannot be right because, while this double sulphide is decomposed by water furnishing a clear soln. of sodium carbonate, the precipitate retains variable quantities of sodium sulphide, and, if

oxygen be present, sodium thiosulphate is formed; with carbon dioxide, also some hydrogen sulphide is always evolved. A. W. Hofmann has reported:

Although E. Kopp's process is irreproachable so far as regards the conversion of sodium sulphate into carbonate (this is certainly not the case !), yet it is very defective with respect to the re-utilization of the sulphur; his sulphide of iron contains too much sodium sulphide to yield, when burnt, any considerable quantity of SO_2, which, moreover, is accompanied by an enormous bulk of nitrogen, corresponding to the oxygen combining with the iron and the sodium sulphide. Its utilization in vitriol-chambers would be out of the question.

M. Waldeck has also shown that the wear on the fireclay or cast-iron linings of the furnace is very severe and costly, this fact, coupled with the bad yields, explains why E. Kopp's process could not succeed against N. Leblanc's process. J. Bowron and G. Robinson (1863), T. Macfarlane (1863), J. Hargreaves and T. Robinson (1872–3), M. Lételié (1891), and P. C. Don (1870) patented modifications of E. Kopp's or Père Malherbe's processes. H. M. Baker (1870) heated salt-cake with coal and clay or alumina to form sodium aluminate which was decomposed with carbon dioxide for aluminium hydroxide and sodium carbonate. C. R. Claus (1869) proposed desulphurizing sodium sulphide by heating a mixture of eq. quantities of sodium fluosilicate and sulphide in steam: $Na_2SiF_6+2Na_2S+2H_2O=6NaF+SiO_2+2H_2S$. The hydrogen sulphide is collected and utilized, and the mixture of silica and sodium fluoride is treated with calcium hydroxide or carbonate to form respectively soluble sodium hydroxide or carbonate, and insoluble calcium fluoride mixed with silica. The insoluble residue is mixed with hydrochloric acid and then with sodium chloride and sodium fluosilicate is regenerated.

R. Laming (1859) proposed passing a current of steam and air through a heated mixture of coal and sodium sulphate until no more hydrogen sulphide escapes, and then recovering the sodium carbonate by lixiviation. A. Vogt and A. Figge treated porous briquettes, made of salt-cake with clay or lime, or magnesia or silica, at a red heat with carbon monoxide to reduce the sulphate to sulphide, and then with carbon dioxide to convert the sulphide to carbonate. A. Kayser, A. B. Young, and H. Williams (1885) claimed that a mixture of carbon monoxide and dioxide converts sodium sulphate, at a dark red heat, into sodium carbonate. W. Smith and W. B. Hart did not get good results. G. Lunge has also reported on the process as applied on the Hautmont Chemical Works. C. R. Claus (1886) and G. E. Davis (1887) used water gas for reducing the sodium sulphate to sulphide; and used carbon dioxide alone or with steam for converting the sulphide to sulphate. A. E. Fletcher (1873) also reduced sodium sulphate by heating it in reducing gases, and converted the sulphide to carbonate by carbon dioxide. A. G. Haddock and J. Leith (1890) converted the calcium sulphide, CaS, in alkali waste to the hydrosulphide, $Ca(SH)_2$, by treating a slurry of the waste with hydrogen sulphide. Conc. soln. of sodium sulphate and calcium hydrosulphide gave a precipitate of calcium sulphate and a soln. of sodium hydrosulphide which is converted by carbon dioxide into sodium carbonate. Half the escaping hydrogen sulphide is used for converting a fresh quantity of alkali waste, and the other half is available for other uses. Thus half a given quantity of salt-cake is worked up by the Leblanc process, and half by the proposed process. The process offered many theoretical advantages which did not materialize in practice.

J. A. C. Gren observed that an aq. soln. of sodium sulphide is decomposed by carbon dioxide forming sodium carbonate with the evolution of hydrogen sulphide; and if the stream of carbon dioxide be continued, sodium bicarbonate is formed. Over fifty patents based upon these observations were obtained. E. Berl and A. Rittener have studied the action of carbon dioxide upon sodium and calcium sulphides. The reaction is by no means simple, for a great proportion of the sodium is converted into bicarbonate before the whole of the sodium sulphide has been decomposed; indeed, hydrogen sulphide still escapes even in the advanced stage of the process, where the sodium is almost entirely present as bicarbonate, and the

sulphide is completely decomposed only when all the sodium has been converted into bicarbonate. Carbonic and hydrosulphuric acids are of nearly equal strength, and the effects are influenced by the mass action of each. The first stages in the actions of carbon dioxide on sodium sulphide and hydrogen sulphide on sodium carbonate furnish the same products: $Na_2S+CO_2+H_2O=NaSH+NaHCO_3$; and $Na_2CO_3+H_2S=NaHS+NaHCO_3$. There is then a balanced reaction: $NaHCO_3+H_2S \rightleftharpoons NaSH+CO_2+H_2O$; at higher temp. sodium carbonate as well as sodium bicarbonate, appears, and sodium sulphide, as well as sodium hydrosulphide, is formed. The constant of division K in the condition of equilibrium: $[NaHCO_3][H_2S]=K[NaHS][H_2CO_3]$, is 2·16 at 14°, and it diminishes with a rise of temp. which thus favours the formation of sodium hydrosulphide—at 18°, K=2·01 to 1·98; at 55°, K=0·90; at 60°, K=0·90; and at 90°, K=0·56. It was also observed that when 30 per cent. carbon dioxide is used for decomposing the sodium sulphide, the proportion of hydrogen sulphide in the gas phase remains almost to the end of the reactions above the minimum required for the combustibility of hydrogen sulphide to sulphur dioxide and water, whereas in the action of carbon dioxide on sodium sulphide, this limit is exceeded only in the early stages.

The fact that in order to convert sodium sulphide to the carbonate, H. L. Duhamel du Monceau and A. S. Marggraf treated sodium sulphide with acetic acid, and ignited the product for the carbonate, is of mere historical interest. W. Gossage (1870) proposed superheated steam; J. Wilson used sodium bicarbonate: $Na_2S+2NaHCO_3=2Na_2CO_3+H_2S$. Although several patents—C. F. Werckshagen, and C. Böhringer and G. Clemm—have been obtained for this principle, the reaction is incomplete, and requires a large excess of the carbon dioxide. J. Pedder (1894) heated the sulphide with coal: $2Na_2S+2C+5O_2=2Na_2CO_3+2SO_2$. C. M. T. du Motay (1870) used sodium or calcium hydroxide; R. Laming (1859) used ammonium carbonate, G. Clemm (1853) used magnesium carbonate. G. E. Habich (1856), T. Cottrill (1853), and R. de la Souchère (1878) used native iron carbonate; but that mineral acts too slowly and incompletely to be of much practical use. R. von Wagner (1865) and E. Siermann (1878) proposed to use alumina. A. R. Arrott (1859) patented the use of ferric or manganic oxide in the wet way, and modifications were patented by W. Gossage (1859), J. Wilson (1838); and P. Lemoult (1907) and F. Ellershausen (1890) used sodium ferrite, $Na_2O.Fe_2O_3$, which acts much more quickly than ferric oxide. W. H. Clayfield (1804) proposed to use lead, zinc, or their oxides for converting alkali sulphates into the hydroxides and ultimately into the carbonates. L. Possoz (1858), E. A. Parnell (1870), C. Crockford (1871), and F. P. E. de Lalande (1887) also recommended zinc oxide for the desulphurization of sodium sulphide, and H. W. de Stucklé (1904) recommended sodium zincate. In 1829, C. P. Prückner obtained a prize offered by the Academy of Science of St. Petersburg for the following process:

Sodium chloride with ammonium sulphate is decomposed into sodium sulphate and ammonium chloride. By ignition with coal the sulphate is reduced to sulphide; and its soln. is boiled with coppersmiths' scales (Cu_2O) till all the sulphur has been precipitated as copper sulphide and only caustic soda remains. The former, by gentle roasting, is converted into cupric sulphate, or more strongly heated till only CuO remains; the escaping SO_2 is conducted into ammonia-liquor, obtained by heating the ammonium chloride of the first operation with lime. The ammonium sulphite remains in contact with the air till it has been converted into sulphate, and can serve for again decomposing common salt.

Patents for somewhat analogous process were obtained by M. Poole (1839), W. Hunt (1840), M. W. Johnson (1852), F. A. Bazin and M. Wilden (1876), and E. M'Clintock (1861).

The preparation of alkali carbonate from alkali nitrate.—The sodium nitrate required for the manufacture of nitric acid, and for the sulphuric acid chambers is converted into nitre-cake—sodium acid sulphate, and is utilized as salt-cake in making alkali. Many of the proposals for converting sodium nitrate into the carbonate, really aim at getting the alkali as a by-product in the manufacture of

nitric acid, in a more convenient form for converting it with the hydroxide or carbonate. H. L. Duhamel du Monceau (1735),[11] and A. S. Marggraf (1762) knew that when a mixture of coal and nitre is deflagrated and the product lixiviated with water, a soln. of sodium carbonate is formed. F. Brown (1884) and A. and G. Freda and M. Patroni (1890) patented the manufacture of alkali carbonates from nitrates and charcoal.

H. W. F. Wackenroder prepared what he called *nitrum fixum* either by projecting powdered charcoal in small portions at a time on fused nitre until detonation no longer occurs, or by adding a mixture of nitre with one-third its weight of charcoal in small portions at a time to a red hot crucible. The resulting carbonate extracted with water contains some nitrite, silicate, and cyanide as impurities. E. Riegel and J. Zinkeisen used a similar process, and calcined the mixture 15 min. H. W. F. Wackenroder also made what he called *fluxus albus*, or *white flux*, by igniting a mixture of equal parts of potassium tartrate and nitre; the product is white, and since insufficient carbon is present to reduce all the nitrate—the product contains both nitrate and nitrite, as well as carbonate: if twice as much tartrate be used, the product was called *fluxus niger*, or *black flux*. The potassium carbonate can be extracted from the mass with water. H. W. F. Wackenroder found the product contained some cyanide, but some cyanate was also present.

By decomposing sodium nitrate at 800°–900° with hydrocarbon gases, H. E. Baudoin and E. T. H. Defort propose to make sodium carbonate, ammonia, and carbon dioxide. C. Wöllner proposed decomposing the nitrate by ignition with copper; E. Pollacci, with iron; W. C. Brown, with lead; and D. Hill, with zinc. L. Mond (1862) proposed preparing nitric acid by heating sodium nitrate with basic or indifferent substances like the oxides of iron, manganese, copper, cobalt, or nickel, and working the residues for sodium hydroxide. F. M. Lyte used ferric oxide; G. Lunge and F. M. Lyte manufactured white lead, and obtained sodium hydroxide as a by-product. F. Wöhler showed that the ignition of a mixture of sodium nitrate and manganese dioxide, without access of air, gives a lower oxide of manganese and sodium hydroxide without a trace of sodium manganate being formed; J. R. Glauber (1648) reported that the ignition of a mixture of saltpetre and clay gives nitric acid; F. Reich also noted that the nitrate is decomposed by silica; and R. von Wagner, by alumina—in the one case sodium silicate, and in the other case sodium aluminate are formed; and in both cases nitric acid is given off. The solids can be converted into sodium hydroxide and silica or alumina respectively by treatment with carbon dioxide. Patents were obtained by H. M. Baker, J. H. Poole, and W. R. Stace, and by W. Garroway for similar processes. One difficulty is to obtain a suitable refractory capable of withstanding the corrosive action of the fused mixtures. A similar objection applies to attempts to treat a heated mixture of sodium nitrate and calcium carbonate by steam as proposed by I. Walz and by K. Lieber. Almost the theoretical yield of nitric acid is obtained, and the mixture of sodium carbonate and lime used for making sodium hydroxide. G. Lunge found even platinous vessels were destroyed in a short time. A. Vogt heated sodium nitrate with quicklime in a stream of steam and carbon dioxide at 350°. The nitrous fumes escape and are oxidized to nitric acid; the lixiviation of the residue gives sodium carbonate. W. Garroway used a similar process with quicklime, baryta, strontia, or magnesia and sodium nitrate. F. Kuhlmann heated a mixture of sodium nitrate and magnesium or calcium sulphate; the nitrous fumes which escaped were oxidized to nitric acid, and sodium sulphate was obtained as a by-product. M. Leuchs (1844) was the first to propose making potassium nitrate by the mutual decomposition of soln. of chemically eq. quantities of sodium nitrate and potassium carbonate, $K_2CO_3+2NaNO_3 \rightleftharpoons 2KNO_3+Na_2CO_3$, and details of the process have been described by E. G. Gentele, F. Kuhlmann, P. Bolley, C. Wöllner, G. Schnitzer, C. Schwarz, and H. Grüneberg. G. Lunge also suggested the manufacture of potassium nitrate by the actions of potassium hydroxide on sodium nitrate, with sodium hydroxide as a by-product. There is an impracticable suggestion patented by F. S. M. de Sussex to decompose sodium chloride by nitric

acid, and convert the sodium nitrate into carbonate. There are also proposals to apply the ammonia or Solvay process to sodium nitrate by G. T. Gerlach (1876), A. M. and J. F. Chance (1885), and A. Colson (1910).

The preparation of the alkali carbonates by the electrolysis of solutions of the chlorides.—The methods of preparing the alkali carbonates by the electrolysis of soln. of the chlorides has been in part discussed in connection with the electrolysis of these soln. for chlorine, chlorates, and the alkali hydroxides. Modifications are required for carbonating the caustic alkali. J. Marx[12] and W. Hempel showed that if a current of carbon dioxide be passed in the cathode liquid during the electrolysis of sodium chloride, chlorine and sodium carbonate are formed; the hydrogen formed at the same time can be combined with the chlorine to produce hydrochloric acid. T. Parker and A. E. Robinson suggested keeping fatty acids in the cathode chamber during the electrolysis of a soln. of sodium chloride and decomposing the soap which rose to the surface by carbon dioxide. E. Hermite and A. Dubosc electrolyzed the alkali chloride soln. in the presence of alumina or aluminium chloride so that alkali aluminate was formed at the cathode. The salt was there decomposed by carbon dioxide. W. Spilker and C. Löwe placed an anode in a soln. of alkali chloride, the cathode in one of alkali carbonate; a fresh soln. of the alkali chloride was continuously introduced into the former, and carbon dioxide into the latter. Chlorine was produced at the anode.

The impurities in commercial alkali carbonates.—Sodium carbonate prepared by Leblanc's process may have sulphate and chlorides as impurities as well as thiosulphates, ferrocyanides, and calcium carbonate. Cryolite soda may have alumina. G. H. Bauer[13] found magnesium carbonate in some commercial soda; R. Fresenius, arsenic and selenium; H. Wurtz, silicate and phosphate; A. le Ricque de Monchy, organic matter; C. F. Rammelsberg and A. Baumgarten, vanadium and fluorides; A. Lecrenier, titanium, molybdenum, tantalum, nickel, and cobalt. If the alkali carbonate is free from *salts of the heavy metals*, aq. soln. (1 : 20), acidified with hydrochloric acid, will not be affected by soln. of hydrogen sulphide; if free from *chlorides*, the aq. soln. acidified with nitric acid, will not give an opalescence with silver nitrate; if free from *sulphates*, the aq. soln. when acidified with hydrochloric acid, and boiled with a soln. of barium chloride, will give no turbidity on standing some hours; and if free from *sulphides*, *sulphites*, or *thiosulphates*, the yellowish-white precipitate obtained by pouring one c.c. of the aq. soln. into 10 c.c. of $\frac{1}{2}N$-silver nitrate soln. should not become darker in colour (grey, brown, or black) when heated to 60°–70°. The presence of *nitrates* is detected by the ferrous sulphate test; and *phosphates*, by the ammonium molybdate test. Potassium *cyanide* is detected by dissolving 0·5 grm. of ferrous sulphate in 5 c.c. of water, adding 5 c.c. of a 5 per cent. soln. of the carbonate, and one or two drops of ferric chloride, warming to 60° or 70°; and acidifying the soln. with hydrochloric acid. A green coloration or a blue precipitate should not appear. To test for *silica*, evaporate to dryness a soln. of 5 grms. of the carbonate with 20 c.c. hydrochloric acid and 20 c.c. of water; dry the residue at 120°, and dissolve in a soln. 25 c.c. of water and 3 c.c. of hydrochloric acid; the soln. should be clear. To test for *alumina*, add 12 c.c. aqua-ammonia to a soln. of 5 grms. of potassium carbonate in 25 c.c. of water, and 25 c.c. of dil. acetic acid, and warm the mixture for half an hour on the water-bath—no precipitation should occur. The alkaline soln. will give no turbidity with oxalic acid if calcium salts be absent. *Ammonium salts* are detected by Nessler's test; *arsenic*, by Marsh's test; *iron salts*, by the ammonium thiocyanate test.

The purification of sodium carbonate.—According to J. L. Gay Lussac, sodium carbonate is obtained of a high degree of purity by repeatedly crystallizing the commercial salt. The soln. obtained by dissolving the crystals in a little water, is boiled and treated with $\frac{1}{1000}$th part of calcium hydroxide, and the clear soln. is then recrystallized until the crystals are free from sulphate and chloride. The soln. is best agitated when the crystals are forming, so that the finely granular product is

more easily separated from the less pure mother liquid. The anhydrous carbonate is best obtained from the hydrocarbonate because the hydrated carbonate during ignition first melts in its water of crystallization, and consequently gives some trouble, and also because the hydrocarbonate has a low solubility in water, and can be readily obtained free from sulphates and chlorides by washing the granular salt with distilled water, or by recrystallization from a soln. of the salt in five times its weight of water.

A. Gawalowsky purified the commercial salt by boiling it with freshly precipitated lead carbonate, adding sodium hydrocarbonate to the decanted liquid, and evaporating in vacuo, when sodium hydrocarbonate crystallizes out. The mother liquid is evaporated, and the first washings rejected. The main fraction is redissolved, crystallized from water with refined wood charcoal, and filtered through platinum wool.

The preparation of lithium carbonate.—C. G. Gmelin [14] noted that transparent lithium hydroxide gradually becomes opaque on exposure to the air owing to the absorption of carbon dioxide. J. J. Berzelius prepared **lithium carbonate,** Li_2CO_3, by adding barium acetate to a soln. of lithium sulphate, evaporating the filtered liquid to form lithium acetate, and calcining the acetate to form the carbonate; L. Troost treated with carbon dioxide the lithium oxide obtained by heating a mixture of lithium nitrate and copper. J. J. Berzelius also prepared lithium carbonate by treating a conc. soln. of lithium chloride with an excess of ammonium carbonate, and washing the precipitated carbonate with alcohol. J. S. Stas employed the last-named process, for he poured a soln. of lithium chloride (1 : 1) into an excess of a soln. of ammonium carbonate in aqua ammonia, and heated the mixture on a water-bath so long as the precipitate did not increase in bulk. About half the lithium in the original soln. was thus obtained as a granular precipitate; if the precipitation be made in the cold, about one-third is obtained in a slimy form difficult to wash. The granular precipitate was washed with dil. ammonia. If the precipitation be made with sodium or potassium carbonate, L. Troost showed that these alkalies cannot be removed by washing. To purify the lithium carbonate so obtained, L. Troost and J. S. Stas both recommended dissolving it in water through which a stream of carbon dioxide is passed, and then boiling the soln. Crystalline lithium carbonate is precipitated. It is to be dried at 200°. F. Stolba has also described a method of purifying the salt. The slow evaporation of aq. soln. of lithium carbonate gave A. Arfvedson small prisms; L. Kralovansky, small cubes. F. A. Flückiger also obtained crystals a millimetre long by evaporating on the water-bath. a soln. sat. at 15°.

The preparation of rubidium and cæsinm carbonates.—R. Bunsen [15] made rubidium carbonate by treating rubidium sulphate with barium hydroxide, and evaporating the filtrate to dryness with ammonium carbonate, when crystals of the carhonate separate. R. Bunsen also transformed rubidium chloride into carbonate by first heating the chloride with nitric acid to convert it into the nitrate, and then treating the latter with an excess of oxalic acid. The oxalate is converted to carbonate by calcination. H. L. Wells made cæsium carbonate by L. Smith's process, *viz.*, by evaporating to dryness a mixture of cæsium nitrate with twice as much oxalic acid, dissolved in a little water, and calcining the residue in a platinum crucible. Cæsium carbonate forms a syrupy liquid which crystallizes with difficulty.

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§ 29. The Manufacture of Soda by N. Leblanc's Process

The manufacture of soda is one of the greatest if not the greatest of the benefits which modern science has conferred upon humanity.—A. ANASTASI.

Near the end of the eighteenth century the difference between the two fixed alkalies—potassium and sodium carbonates—was known; sodium carbonate *barilla* was largely made from the ashes of sea plants, and potash from the ashes of land plants. The Arabs also had brought some natural soda into Europe, *viâ* Spain. These sources were not sufficient to cope with the demand for alkali for the manufacture of soap, glass, etc. Potash was at that time the cheaper and dominant alkali. With the steadily increasing demands for alkali and the very limited sources of supply presented by the incineration of wood, many attempts were naturally made to substitute the base of common salt, because that with a suitable method of extraction nature has provided inexhaustible, abundant, and cheap

stores of that salt as a raw material. The quest for a cheap method of extracting the basal alkali from common salt was stimulated by the offer of a prize of 2400 livres by *l'Académie des Sciences* of Paris in 1775, for the manufacture of artificial soda from common salt. The first claimant was Père Malherbe in 1778, who calcined a mixture of sodium sulphate, metallic iron and charcoal in a reverberatory furnace, and extracted the soda from the cold product by lixiviation with water. A factory was started at Javel in 1779, but was short-lived.

In 1781, Bryan Higgins patented a similar process in London; in this, sodium sulphate was melted with charcoal and then mixed with iron or other metals. A day after B. Higgins' patent, A. Fordyce patented a similar process in which iron oxide—the calx of iron—was used instead of iron. G. de Morveau and M. Carny erected a factory for making soda by a process based on C. W. Scheele's observation that when a mixture of common salt and lime is exposed to the air, an efflorescence of soda gradually develops on the surface. About the same time, M. de la Métherie proposed to ignite sodium sulphate with coal, and to extract the carbonate from the product. The sulphurous vapours given off were to be used for the manufacture of sulphuric acid for converting the sodium chloride into sulphate. Unfortunately, sodium sulphide, not carbonate, is the main product of the reaction. None of the factories erected for the application of these processes had any success, and could not compete with barilla in price or quality.

M. de la Méthérie's impractical process suggested to Nicolas Leblanc, about 1787, the proper soln. of the problem, and, after a favourable report had been made by J. P. J. d'Arcet in 1790, a works was erected at St. Denis under the patronage of the Duke of Orleans. A sealed description of N. Leblanc's process was deposited with the notary on March 27, 1790; and a patent was granted to N. Leblanc on September 25, 1791. The essential features of the process therein described are not very different in principle from the process as used to-day:

100 lbs. of anhydrous sodium sulphate, 100 lbs. of pure limestone or chalk from Mendon, and 50 lbs. of charcoal are crushed and mixed between iron rollers. The mixture is spread out in a reverberatory furnace, the working-holes are closed, and fire is applied; the substance gets into a pasty condition, froths up, and is converted into soda, which is only distinguished from the soda of commerce by a higher strength. The mass must be frequently stirred up during the fusion, for which iron rakes, spatulas, etc., are employed. From the surface of the fluxing mass a large number of flames break forth similar to the flame of a candle. As soon as this phenomenon begins to cease, the operation is finished. The batch is then drawn out of the furnace with iron rakes, and can be collected in any kind of moulds in order to give it the shape of the commercial blocks of soda. The operation may also be carried on in closed vessels, such as crucibles, but thereby becomes more costly. The proportions of the raw materials may be changed; for instance, less limestone and coal may be taken; but the above proportions have given the best results. The quantity stated furnishes upwards of 150 lbs. of soda.

The factory prospered very well until 1793, when the Duke of Orleans was guillotined by the French Revolutionists, and the works confiscated and scattered by public sale. The isolation of the French as a consequence of the revolutionary wars cut off the supplies of potash, and curtailed those important industries dependent on this raw material. The *Comité de salut public* issued an appeal to the French chemists to utilize all materials natural to their own country so as "to render abortive the efforts and hatred of despots"; this committee also annulled N. Leblanc's patent, and, for the benefit of the state, compelled N. Leblanc [1] to make known his process for manufacturing soda. The tragic story of the ruin of N. Leblanc is told by A. Anastasi in his work *Nicolas Leblanc, sa vie, ses travaux et l'histoire de la soude artificielle* (Paris, 1884). Although N. Leblanc fairly won the Academy's prize, it was never paid over to him; nor did he receive any more than the mockery of a compensation for the confiscation of his works and his process. N. Leblanc, in the bitterest poverty and despair, died by his own hand January 16, 1806; eighty years later a statue was erected to his memory in the Conservatoire des Arts et Métiers, at Paris!

Other alkali works using N. Leblanc's process were started in Paris, Dieuse, Thann, Chauny, Alais, and Marseilles—the centre of the French soap industry. These works were more successful. In England, W. S. Losh, of Walker-on-Tyne, visited France during the Peace of Amiens (1802), and there learned necessary details about N. Leblanc's process, and, in 1814, he made small quantities of soda by the French process. C. Tennant, of St. Rollox, introduced the process in 1818. The salt tax, at that time £30 per ton, hindered the development of the soda industry, and when that tax was repealed, James Muspratt commenced the manufacture on a large scale. This was done in 1823. There was a difficulty at first with the soap-makers accustomed to work with barilla and kelp alkali. Although the new soda was purer and stronger, prejudice had to be overcome by J. Muspratt giving away large quantities. Once the soap-maker's recipes had been adapted to the new soda, the demand for the Leblanc soda was very great. Apart from a few works in the Midlands and Scotland, the alkali industry is concentrated in South Lancashire and Tyneside, where coal and salt were close at hand. In Germany, the first Leblanc soda was made at Schönebeck near Magdeburg—the output in 1843 was 200 tons per annum—another small works was established at Ringkuhl near Cassel, and later still, numerous alkali works were established in various parts of the country. The first alkali works in Austria was erected in 1851 at Hruschau (Moravia); a second one, about the same time, at Petrowitz (Silesia); and another, the largest of all, at Aussig in 1856. The Leblanc soda process for the conversion of common salt into sodium carbonate involves three major operations: (1) The conversion of sodium chloride to the sulphate—salt-cake process. (2) The conversion of the sulphate to black ash—a mixture of calcium sulphide, sodium carbonate, etc. (3) The extraction of sodium carbonate from black ash by lixiviation with water and subsequent crystallization from the aq. soln. The various operations have been described in much detail in G. Lunge's *A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali* (London, 1895).

(1) Conversion of sodium chloride into sodium sulphate—salt-cake—The first stage in the process is to convert the sodium chloride into sodium sulphate by the action of sulphuric acid.

Half a ton of salt is charged into large iron pans—9 to 10 ft. in diameter, and 2 ft. deep—and an equal weight of sulphuric acid of sp. gr. 1·7, from Glover's acid tower is run into the pan from a lead cistern. The pan is heated by hot gases from adjacent furnaces, when torrents of hydrogen chloride—*pan-gas*—are given off. The reaction is mainly that symbolized: $H_2SO_4+NaCl=NaHSO_4+HCl$. 65 per cent. of the hydrochloric acid escapes through a flue and is absorbed by water to form *pan-acid*. Good cast-iron pans will stand several thousand charges before they are eaten through; the cast iron should be of uniform composition and free from graphitic carbon and silica. If salt-cake is desired very free from iron—*e.g.* for making special forms of glass—leaden pans are used—but these are costly, and liable to melt if slightly over-heated. The residue is then raked from the pans into the hearth of a reverberatory furnace, or, in the more modern furnaces, in order to avoid contamination with fuel ash, the residue in the pan is raked into a muffle or *blind-roaster*, where the mixture is roasted at a higher temp. while it is stirred with iron rakes. Here the reaction is that represented by the equation: $NaCl+NaHSO_4=Na_2SO_4+HCl$. The escaping hydrochloric acid—*roaster gas*—escapes through a flue and is absorbed separately—*roaster acid*. The product in the furnace is discharged into iron trucks. About twelve charges are worked in each furnace every day. The style of muffle usually employed is the so-called *plus pressure furnace* devised by W. Deacon in 1876. This is intended to prevent the escape of hydrogen chloride through any leaks in the walls of the muffle whereby the gas passes into the flues and thence into the atm. without condensation. This is effected by making the draught stronger inside the muffle than in the surrounding flues; otherwise expressed, there is a greater press.—plus press.—in the flues than in the muffle. If there is a leak in the muffle therefore a little flue gas will enter the muffle when it does comparatively little harm, and stops complaints about the escape of hydrochloric acid from the chimneys.

Many attempts have been made to carry out the operations automatically in mechanical furnaces so as to avoid the disagreeable operation which attends the unavoidable escape of pungent acid vapours through the working doors during the stirring up of the charge in pan or roaster. The most successful of these is the furnace devised by J. Mactear in 1879. This furnace has a circular revolving bed covered by a fixed arch. The furnace gases pass

between the revolving bed and the fixed arch. The mixture is fed continuously into the middle of the bed and is raked by fixed stirrers towards the circumference, and finally drops over. The action is continuous so that the hydrochloric acid is evolved at a uniform speed. The acid-gas mixed with the flue gases, passes on to the cooling plant. The Hargreaves process for salt-cake—*vide* sodium sulphate—can also be used.

The product of this reaction is sodium sulphate, also called *salt-cake*, which occurs in trade as a more or less granular mass, with more or less fused lumps. The latter may contain undecomposed sodium chloride in the cores. The colour is yellowish or greenish-white—often white. G. E. Davis' analyses [2] of salt-cake are:

Salt-cake from	Na_2SO_4	$CaSO_4$	$FeSO_4$	NaCl	SO_3	H_2O	Insoluble sand
Blind roaster . .	94·39	1·14	0·68	2·63	0·95	0·09	0·11
Open roaster . .	96·14	1·15	0·56	0·23	1·82	--	0·07
Hargreaves' . .	97·82	1·05	0·52	0·74	0·02	—	0·04

G. E. Davis' figures are rounded off to the second decimal, which even then represents a greater accuracy than is possible by the methods of analysis available. The presence of both free sulphuric acid and undecomposed sodium chloride is largely due to the fact that the reaction: $2NaCl+H_2SO_4=Na_2SO_4+2HCl$, is reversible, and would require a larger excess of sulphuric acid than is convenient to make it complete.

(2) **The conversion of salt-cake into black ash.**—J. B. A. Dumas first attempted to explain the reaction in the black-ash furnace; and his hypothesis was in vogue with slight modifications for many years. J. B. A. Dumas started from the wrong assumption that calcium sulphide is readily soluble in water, because neither hydrogen nor ammonium sulphides cause a precipitate in a soln. of calcium chloride. He then argued that if calcium sulphide were present in black ash, the subsequent lixiviation with water would set up a reaction between the calcium sulphide and sodium carbonate: $Na_2CO_3+CaS=Na_2S+CaCO_3$; consequently, J. B. A. Dumas inferred that not calcium sulphide but an insoluble calcium oxysulphide, 2CaS.CaO, is formed as was previously suggested by L. J. Thénard. The supposed calcium oxysulphide is assumed to be insoluble in water in order to account for the retention of the sulphur by the insoluble residue and the non-appearance of considerable amounts of sodium sulphide in the water used in the lixiviation of the black ash. He represents the initial and end-stages of the reaction by the equation: $2Na_2SO_4+3CaCO_3+9C=2Na_2CO_3+CaO.2CaS+10CO$.

In 1847, B. Unger also investigated the subject, and agreed in the main with J. B. A. Dumas' [3] hypothesis; he assigned the formula CaO.3CaS to the supposed oxysulphide because H. Rose had previously prepared an analogous compound. In a later paper, B. Unger devised a series of reactions in which steam played a vital part, but A. Scheurer-Kestner showed that black ash can be made in a closed crucible with thoroughly dried materials. A. C. Brown also supported the Unger-Dumas hypothesis in assuming that the coal first reduced the sodium sulphate to sulphide: $Na_2SO_4+4C=Na_2S+4CO$; and that the sodium sulphide reacts with the calcium carbonate, forming sodium carbonate and calcium oxysulphide: $3Na_2S+4CaCO_3=3Na_2CO_3+CaO.3CaS+CO_2$. J. W. Kynaston cast doubts on the oxysulphide theory by showing that the alleged compound could not possess the stability in water ascribed to it by J. B. A. Dumas.

In 1861, W. Gossage showed that calcium sulphide is insoluble in water, and is but little attacked by sodium carbonate; he also showed that the residue left after the lixiviation of black ash is a mixture of calcium monosulphide and carbonate, even when no sodium sulphide is present in the liquor; and that if any sodium sulphide be present in the liquor, it is derived from the formation of calcium polysulphides in the black ash which can be prevented by using an excess of limestone. Both J. W. Kynaston and W. Gossage showed that no sodium hydroxide is present in black ash because (*a*) sodium hydroxide melted with black ash forms calcium oxide and sodium carbonate; and (*b*) no sodium hydroxide can be extracted with

alcohol. W. Gossage expressed the reactions in the formation of black ash by the equation: $2Na_2SO_4+3CaCO_3+9C=2Na_2CO_3+2CaS+CaO+10CO$, although he did not believe this carbon all goes away as carbon monoxide. A. Scheurer-Kestner also adopted Gossage's views, and showed that in the main reaction no carbon monoxide is formed; he supposed that in the first stage of the reaction the sodium sulphate is reduced by carbon to the sulphide: $Na_2SO_4+2C=Na_2S+2CO_2$; and that the calcium carbonate then reacts with the sodium sulphide to form sodium carbonate and calcium sulphide: $5Na_2S+7CaCO_3=5Na_2CO_3+5CaS+2CaO+2CO_2$; and that the carbon monoxide which appears towards the end of the operation when the temp. is much higher, is due to the action of coal on the limestone: $CaCO_3+C=CaO+2CO$. A. P. Dubrunfaut accepted A. Scheurer-Kestner's explanations, but assumed the equation: $Na_2SO_4+CaCO_3+4C=Na_2CO_3+CaS+4CO$, which is erroneous in stating that carbon monoxide, not carbon dioxide, is the gaseous product of the reaction.

About 1865, E. Kopp, and P. W. Hofmann tried to revive the oxysulphide theory, but J. Pelouze refuted their arguments; and after a long study of the reactions, J. Kolb confirmed A. Scheurer-Kestner's work, but concluded that in the main reaction the calcium carbonate loses its carbon dioxide by the action of the carbon dioxide in the fire gases. A. Scheurer-Kestner then showed that in this last conclusion J. Kolb is in error, because black ash can be made in crucibles without any assistance from the fire gases; that the decomposition of the calcium carbonate, even in the presence of coal, requires a higher temp. than the reduction of the sodium sulphide; and that black ash is obtained by directly heating sodium sulphide with calcium carbonate.

A. Scheurer-Kestner's theory of the major changes which go on in the black-ash furnace is thus a simple one:

The mixture occupies a depth of several inches on the furnace-bed. Its upper portions are first reduced, and that to a considerable extent before the surface is renewed by working with the tools. The quicklime which had formed in the pasty layer at the surface is again converted into carbonate by the CO_2 arising from the reduction of sodium sulphate in the lower layers. At the moment when the sodium sulphide fuses, it penetrates the chalk, and they are mutually decomposed. When all the sulphate has been reduced and the evolution of CO_2 becomes less, the temp. of the mass rises and the calcium carbonate in excess begins to decompose with evolution of CO. The evolution of this gas is a valuable sign for marking the completion of the operation. Since it only occurs when the mass begins to stiffen, it imparts to it that porosity so valuable for lixiviation. If the carbon required for the reduction of the sodium sulphate and the decomposition of the chalk be taken into account, the reaction may be expressed by the following three equations: (i) $Na_2SO_4+2C=Na_2S+2CO_2$; (ii) $Na_2S+CaCO_3=Na_2CO_3+CaS$; and $CaCO_3+C=CaO+2CO$.

The major reactions are complicated by a number of minor or secondary reactions, and by impurities in the raw materials. As a result the black ash may contain 1½ to 2½ per cent. of sodium silicate; ½ to 1½ per cent. of sodium aluminate; 1 per cent. of sodium ferrous sulphide; small proportions of sodium cyanide and thiocyanate derived from the nitrogen of the coal; a relatively small amount of ultramarine; etc. Proposals to use barium carbonate, etc., in place of limestone in the black-ash process are indicated in connection with the preparation of sodium carbonate from sodium sulphide,

The salt-cake is mixed with limestone and coal in the proportions 100, 100, 35·5—the theoretical proportions are 100, 79·4, 16·9. The mixture is heated to a high temp. in a reverberatory furnace which is termed the *balling furnace* or black-ash furnace. The charge is worked on the hearth of the furnace by men with iron rakes. The reaction begins as soon as the mass sinters together, and then progresses rapidly and completely. The end of the operation is indicated by the appearance of yellow flames or "candles" on the surface of the melt—presumably owing to the formation of inflammable carbon monoxide by a reaction between the carbon and the limestone at the high temp. of the furnace: $CaCO_3+C=CaO+2CO$. This evolution of gas makes the lumps or "balls" which are

transferred to iron waggons where they are allowed to cool. The dark-coloured mass is in this stage called *black-ash ball*. The sodium sulphate is reduced by the carbon, and the resulting sodium sulphide reacts with the limestone, forming a mass which when treated with water furnishes calcium sulphide and sodium carbonate. The initial and end-stages of the reaction are symbolized: $Na_2SO_4+CaCO_3+2C=Na_2CO_3+CaS+2CO_2$. In place of the old hand-labour balling furnace, several types of revolving furnace have been devised (Fig. 61). G. Elliot and W. Russell's furnace (1853) was found to give too hard an ash; but the "revolver" patented by J. C. Stevenson and J. Williamson in 1855 was the first successful revolving furnace. Here, the hot gases from the producer gas pass through the

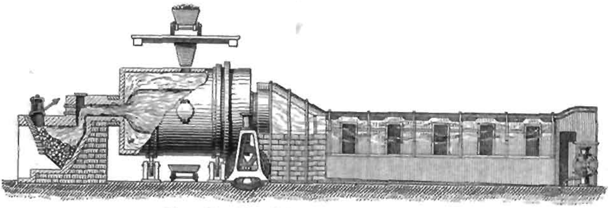


FIG. 61.—Revolving Black-ash Furnace.

cylinder containing the mixture of salt-cake, limestone, and coke. The slow revolution of the cylinder ensures the thorough mixing of the contents. When the yellow flame of carbon monoxide appears, the contents of the cylinder are discharged into iron trucks. The dark-grey or brown porous mass so obtained is called *black ash*. The black ash is allowed to weather for a day or two when it becomes more porous. It is then ready for lixiviation.

In the early days black ash was sent direct to the soap-makers; and for a time was known as *British barilla*. The product deteriorated rapidly when kept, and does not now appear as an article of commerce. Black ash contains 40 to 45 per cent. of sodium carbonate; 30 to 33 per cent. of calcium sulphide; 2 to 6 per cent. of calcium oxide; 6 to 10 per cent. of calcium carbonate. G. E. Davis[4] gives for the analysis of a sample:

SOLUBLE—43·00 per cent.

Na_2CO_3	Na_2O	NaCl	Na_2SO_4	Na_2SO_3	$Na_2S_2O_3$	Na_2S	NaCy	NaSCy
31·81	5·61	2·57	0·19	0·07	0·85	0·16	0·04	0·02

together with sodium aluminate 0·75 per cent., and sodium silicate, 0·91 per cent.

INSOLUBLE—56·47 per cent.

CaS	$CaCO_3$	CaO	FeS	Al_2O_3	SiO_2	MgO	Na_2O	Carbon
28·74	9·27	0·49	0·77	1·04	0·92	0·32	0·57	4·48

together with 0·87 per cent. of sand. G. E. Davis' numbers are here rounded off to the second decimal, since it is doubtful if the analytical methods admit of such a degree of accuracy; the minuteness of the specialization of the constituents also is in some cases of doubtful validity. B. Unger reported in the black ash of the Ringkuhl works: Titanium, 0·015 per cent.; copper and molybdenum, 0·025; phosphorus, 0·023; tantalum, 0·017; fluorine, 0·014; barium, 0·014; nickel and cobalt, 0·013; manganese, 0·013; and lead, 0·013 per cent. A. Scheurer-Kestner found a little selenium in black ash; C. R. Fresenius, arsenic; and C. F. Rammelsberg, vanadium.

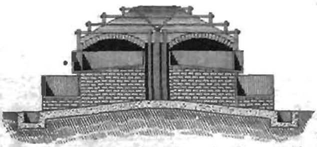


FIG. 62.—Cross-section through Evaporating Pans.

If black ash be exposed to the atm. under ordinary circumstances it soon

exhibits a change. J. Kolb showed that carbon dioxide and moisture are the active agents, since air deprived of these constituents has very little action on black ash between 0° and 100°. Dry carbon dioxide has no more action on dry black ash than it has on quicklime ; but moist carbon dioxide converts the calcium oxide into carbonate, so that no sodium hydroxide is formed, and it also acts on the calcium sulphide, forming calcium carbonate and hydrogen sulphide. Part of the latter escapes, and another part forms calcium hydrosulphide which, with water, forms sodium sulphides—Na_2S and Na_2S_2. Moist air, in the absence of carbon dioxide, is gradually absorbed ; the lime is hydrated ; and the black ash gradually crumbles into fragments, and finally into dust. The sulphides are gradually oxidized to sulphates. The amount of sodium carbonate also gradually diminishes on keeping.

(3) **The extraction of sodium carbonate from black ash.**—The black ash is rapidly lixiviated with warm water so that as little as practicable will be used. The water, below 35°, passes through a series of tanks containing the pulverized mixture. F. Clement and J. B. Désormes' system of washing is based on the fact that the soluble matter dissolves more quickly if placed just below the surface than if placed on the bottom of the vessel, where it is covered by the conc. soln. which prevents contact with the water higher up. Hence, F. Clement and J. B. Désormes placed the material to be lixiviated in perforated vessels just below the level of the liquid. What is erroneously called J. Shanks' lixiviation process is most commonly used. The lixiviation here works on the discontinuous counter-current principle. Fresh water passes through the tank containing the ash which is almost all extracted ; and the water, almost sat., passes through the black ash fresh from the furnace. The liquors are conveyed from the bottom of one tank to the top of another by means of syphon pipes fitted with stopcocks.

The tank liquid is allowed to settle and then conc. by evaporation in shallow pans heated by the waste heat from the black-ash furnace, Figs. 61 and 62. The dark-coloured crystals of monohydrated sodium carbonate, $Na_2CO_3.H_2O$, which separate are fished out with skimmers and recrystallize to form the decahydrated carbonate, $Na_2CO_3.10H_2O$, or else calcined—it is called crude soda ash. The latter is further purified by exposing it to a current of hot air in order to oxidize the sulphides to sulphates. The sulphides impart a slight yellow tinge to the mass. The tank liquid is sometimes treated with carbon dioxide so as to convert the caustic soda and sodium sulphide into sodium carbonate. The soda ash, Na_2CO_3, is then crystallized from water when soda crystals (washing soda) are wanted—$Na_2CO_3.10H_2O$. The carbonate from the Leblanc process has been employed for the production of sodium hydroxide.

The action of water on black ash during the washing involves a complex series of chemical changes which have been studied by J. Kolb, A. Scheurer-Kestner, and J. Pelouze. Calcium sulphide with water gradually forms soluble calcium hydrosulphide : $2CaS+2H_2O=Ca(SH)_2+Ca(OH)_2$. Sodium chloride decreases the solubility of calcium sulphide in water ; sodium sulphate acts in the same direction ; limewater has no perceptible influence on the solubility of calcium sulphide. Sodium carbonate has very little action on calcium sulphide, but the speed of decomposition increases with dilution, time, and temperature. There is no evidence of free sodium hydroxide in normal black ash ; the sodium hydroxide which is found in the tank liquor is due to the action of the free lime of the black ash upon the sodium carbonate, forming sodium hydroxide and calcium carbonate. The causticity of the tank-liquor is not materially altered by the proportion of water, but it increases with the time of digestion and the temp. There are only traces of sodium sulphide in good black ash, but on treating black ash with water varying quantities appear—usually the monosulphide, because the free alkali converts the polysulphides to monosulphide. The proportion of sodium sulphide in the tank liquor increases like the sodium hydroxide with the time of digestion and the temp., but increases very little with an increase in the quantity of water. There is no relation between the amount of sodium sulphide and hydroxide in the tank liquor,

showing that the sulphide is probably formed from the carbonate, not the hydroxide. Consequently, the calcium sulphide reacts with sodium carbonate, forming sodium sulphide and calcium carbonate ; the oxygen of the air oxidizes the calcium sulphide to calcium sulphate, which in turn reacts with sodium carbonate, etc. All these reactions reduce the yield from the process. J. Kolb concluded that in order to get the smallest possible proportion of hydroxide and sulphide in the tank liquor, the black ash should be lixiviated as quickly as possible, with the smallest possible proportion of water, at the lowest possible temp.

F. M. Chance's analysis of the tank-waste, dried at 100° in nitrogen, shows :

CaS	$CaCO_3$	$Ca(OH)_2$	$CaSO_4$	Na_2O	Al_2O_3	FeS	MgO	S
30·17	19·88	1·22	trace	0·84	0·91	0·67	0·43	0·47

with 1·29 per cent. of combined silica ; 8·46 per cent. of coke ; 1·34 per cent. of sand ; and 35·01 per cent. of moisture. The total sulphur present as sulphides of calcium and iron is 13·65 per cent. It will be observed that sulphur is the intermediate agent in converting the chloride to carbonate. It comes in the process as sulphuric acid, and is finally rejected mainly as calcium sulphide in the tank-waste. This sulphur was formerly rejected with the alkali waste which accumulated about the works and became an unmitigated nuisance the more unbearable as the industry increased in magnitude; for in damp weather the hydrogen sulphide which is emitted infects the air for a great distance ; the polysulphides which are leached out by water pollute rivers and streams for miles around. For every ton of soda ash produced there is about 1½ to 2 tons of waste. More than 1000 tons are deposited at Widnes every day ; and it is estimated that 150,000 tons of sulphur valued at £400,000 was annually wasted until a practical soln. of the problem of recovering the sulphur had been obtained.

When exposed to air, the tank-waste soon changes under the influence of oxygen, water, and carbon dioxide. The oxidation of the sulphides may occur so rapidly that the heap becomes red hot, and sulphur dioxide is formed. The action of carbon dioxide, sulphur dioxide, and sulphuric acid on the sulphides liberates hydrogen sulphide. The insoluble calcium sulphide is also oxidized, forming soluble calcium hydrosulphide, $Ca(SH)_2.6H_2O$; polysulphides ; thiosulphate, sulphite, and sulphate ; the corresponding sodium salts are also formed. The subject has been investigated by M. Schaffner,[5] C. Kraushaar, E. Divers and T. Shimidzu, and V. H. Veley. According to E. Divers, the whole oxidation of tank waste consists in the oxidation of hydrogen sulphide which is evolved from it, and which forms water and sulphur. The latter acts on calcium hydroxide, forming calcium pentasulphide, CaS_5, and thiosulphate : $3Ca(OH)_2+12S=CaS_2O_3+2CaS_5+3H_2O$; and in presence of calcium hydrosulphide, $Ca(SH)_2$, the pentasulphide is also oxidized to thiosulphate : $CaS_5+3Ca(SH)_2+6O_2=4CaS_2O_3+3H_2S$.

Various proposals have been made for utilizing tank waste, but many are quite insufficient for dealing with large quantities. It has been proposed as a remedy for dry rot (G. Juncker)[6] ; for potato and vine diseases (F. Liesching) ; for building purposes when mixed with sand, etc. (H. Deacon, F. Kuhlmann, F. Varrentrapp) ; mortar and cement ; bottle glass (G. Lunge) ; asphalt pavement (C. T. Kingzett) ; etc. The more rational treatment of alkali waste is founded on the recovery of the sulphur. G. Lunge thus classifies the various proposals for the recovery of the sulphur :

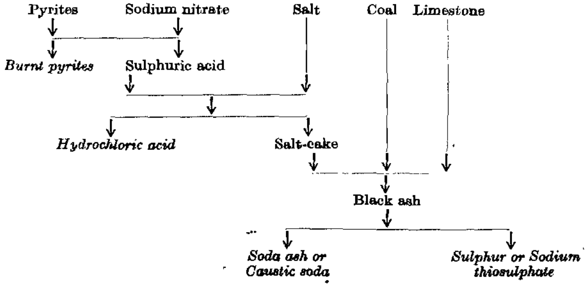
1. Combining the sulphur with iron or in other ways, for example, J. L. Bell[7] made a kind of artificial pyrites by melting tank waste with burnt pyrites along with coke and clay. D. B. Hewitt heated the tank waste with silica to form calcium silicate, and sulphurous and sulphuric oxides which are collected and utilized : H. Bornträger made ferrous sulphide by compressing alkali waste with water and pyrites cinders and burnt the sulphide for the manufacture of sulphuric acid. The Verein Chemischer Fabriken in Mannheim manufactured sodium sulphide from it by exposing a mixture of alkali waste and sodium sulphate to the action of steam under 5 atm. press. The sodium sulphide liquor is easily separated from the calcium sulphate. W. Helbig also boiled the alkali waste with a soln. of sodium

carbonate or tank liquor, and obtained a soln. of sodium sulphide which was crystallized and used in tanning.

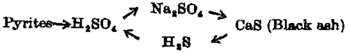
2. Partial recovery of the sulphur by accelerated weathering (oxidation), lixiviation, and decomposition with acids. Sulphur and sodium thiosulphate can thus be obtained. T. H. Leighton lixiviated the oxidized waste and precipitated sulphur from the liquid by hydrochloric acid. W. H. Losh, E. Kopp, J. Townsend and J. Walker, J. L. Jullion, and A. Noble obtained sodium thiosulphate from oxidized tank waste. The oxidation is effected by blowing air and steam through a suspension of waste in coke towers, or by exposing the waste to the air for a week with occasional raking. The calcium thiosulphate which is then leached by water from the oxidized product is converted into sodium thiosulphate by the addition of calcium carbonate. In M. Schaffner, and in L. Mond's process, the alkali waste is treated for the recovery of sulphur. A yellow liquid is obtained from the weathered or oxidized tank waste; the yellow liquid is treated with acid so that all the sulphur, excepting that oxidized to sulphate, is precipitated. The sulphur is then separated from the calcium sulphate by a liquation process. The two processes are fundamentally alike, but differ in detailed procedure.

3. Transformation of the sulphur into hydrogen sulphide and utilization of the latter. In C. F. Claus and F. M. Chance's process, the residue in the tanks remaining after the sodium carbonate has been extracted is dried, finely powdered, and suspended in water. In A. M. Chance's process carbon dioxide is forced through the liquid and hydrogen sulphide is driven off: $Ca(SH)_2+CO_2+H_2O=CaCO_3+2H_2S$. The sulphur is now recovered from the hydrogen sulphide by the catalytic process of C. F. Claus. The hydrogen sulphide mixed with sufficient oxygen to burn the hydrogen, but not the sulphur, is passed into a kiln containing iron oxide. By catalytic action, the iron oxide accelerates the oxidation of the hydrogen sulphide: $2H_2S+O_2=2H_2O+2S$. Most of the sulphur which separates collects as a molten fluid at the bottom of the kiln or in an adjoining brickwork chamber, and is periodically run off. From 65 to 85 per cent. of the sulphur is thus recovered and used again for making sulphuric acid. The oxide of iron is gradually converted into sulphide, and this is perhaps more efficient as a catalytic agent than the original oxide.

A factory in which soda ash is made is called an *alkali works*. A works using the Leblanc process is divided into several departments: (1) The acid works where sulphuric acid is made; (2) Salt-cake works; (3) Black-ash works and lixiviation; (4) White-ash (soda ash) works or caustic soda works; (5) Bleaching powder works where the hydrogen chloride from the salt-cake works is converted into chlorine, and the latter converted into bleaching powder; and (6) Sulphur extraction from tank-waste. The following is a diagrammatic representation of the Leblanc process:



It illustrates the different stages in the manufacture of soda by the Leblanc process. The sulphur cycle in that process is also illustrated diagrammatically by the scheme:



the 15 to 35 per cent. loss of sulphur has to be made good in the form of pyrites for the manufacture of sulphuric acid.

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§ 30. The Ammonia-Soda or E. Solvay's Process

It can hardly be affirmed that the scientific treatment of the ammonia-soda process through recent progress in physical chemistry has given the practical manufacturer any hints on the direction in which he might make his processes more rational and advantageous than before, but there remains the hope that the desired success will be ultimately obtained by a co-operation of theory and practice.—G. LUNGE (1911).

The history of the ammonia-soda process has been the subject of some controversy. It is probable that the basal reaction involved in the ammonia-soda process: $NaCl+NH_4HCO_3 \rightleftharpoons NH_4Cl+NaHCO_3$, was placed before the French tribunal in competition with N. Leblanc's process, but was rejected. Several attempts appear to have been made to deal with the process, but they were not a commercial success until E. Solvay's modification of the process was founded. According to R. Lucian,[1] the letters addressed to A. J. Fresnel show that in 1811 he worked on the preparation of sodium carbonate by the action of ammonium carbonate on sodium chloride. The recovery of the ammonia was not considered at that time, and the invention soon sank into oblivion. A. J. Fresnel himself was fully occupied in researches in optical phenomena. A. Vogel reported that he found a memorandum in his father's note-book dated 1822, in which it is recorded that sodium hydrocarbonate and ammonium chloride are formed when ammonia and carbon dioxide jointly act on a soln. of sodium chloride. According to W. Smith, and L. Mond, J. Thom, in 1836, made about 200 lbs. of soda ash per day by the action of commercial ammonium carbonate on a conc. soln. of sodium chloride, the sodium hydrocarbonate was converted into soda ash, and the ammonia recovered by evaporating the mother liquor, and heating it with lime. According to B. L. Vanzetti, also, G. Forni of Milan, in 1836, made a trial of preparing sodium carbonate by the ammonia process, which he described in a pamphlet, *Della soda arteficiata e nuovo metodo d'estrazione del carbonato di soda* (Milano, 1841). It is doubtful if the work

of A. J. Fresnel, A. Vogel, J. Thom, and G. Forni had any influence on the development of the ammonia-soda process, for it remained entirely fruitless. As G. Lunge has emphasized:

> If the observers themselves do not think it worth the trouble to publish their observations, or else to follow them up on a larger scale, their work is lost for mankind, and does not constitute any claim for being recognized by posterity as the germ of the invention.

The real history of the ammonia-soda process of manufacturing sodium carbonate more properly commences with the patent of H. G. Dyar and J. Hemming on June 30th, 1838. This patent distinctly sets forth the reaction: $NaCl+NH_4HCO_3=NH_4Cl+NaHCO_3$, and describes means of carrying out the operation on a manufacturing scale, so as to recover the ammonia as carbonate for use over and over again. Experimental factories running H. G. Dyar and J. Hemming's process were erected in England, Germany, and Austria, but none were very successful, probably because the operations involved a considerable loss of ammonia. Patents were taken out by A. A. Canning (1840), H. Waterton (1840), W. Chisholm (1862), W. Gossage (1854–5), M. Turck (1854–5), T. Schlösing (1854), H. Deacon (1854), A. E. L. Bellford (1855), T. Bell (1857), and G. H. Ozouf (1864), principally for minor operations connected with the process.

About 1854, T. Schlösing patented a modification of the process, and in conjunction with E. Rolland, started a works at Pukeaux, near Paris, for the manufacture of soda ash by a continuous ammonia process, but the works closed in 1857—probably because of their imperfect mechanical arrangements, and of the ammonia wastage. In 1858, D. Heeren studied the chemical reactions involved in the ammonia-soda process, without advancing the applicability of the process. E. Solvay built a works at Couillet near Charleroi (Belgium) about 1863, and the factory started manufacturing near the beginning of 1865. According to G. Lunge:

> A period of continuous alterations, mishaps, and improvements set in which would have discouraged most other inventors; but E. Solvay held on to his cause in the full belief of its value. . . . It certainly required not merely ordinary energy and pre-eminent mechanical skill, such as Solvay did possess, but an almost fanatical belief in the enormous value of his invention, to battle with many years' failures and heavy losses, till his conception had ripened to its splendid realization.

The factory gradually emerged from the adverse period of induction, such that, in 1869, the plant was doubled, and the output trebled. According to K. W. Jurisch, M. Honigmann erected a small factory near Aachen, using a modification devised by himself, but was not very successful. E. Solvay's process now began to make rapid strides. Other factories were erected in Belgium, France, Germany, Austria, Russia, Italy, America, etc. The Brunner Mond Company's factories in the Northwich district, and at Sandbach near Crewe, are notable. As a result, while but 300 tons were made in the years 1864–68, 1,616,000 tons were made in 1902; and 3,000,000 tons in 1916.

The ammonia-soda process depends upon the fact that when a conc. soln. of sodium chloride is sat. with ammonia, and carbon dioxide is passed through the mixture ammonium hydrocarbonate is formed; this then reacts with the sodium chloride, and sodium hydrogen carbonate is precipitated, and ammonium chloride remains in soln.; the final stage turns on the balanced reaction: $NaCl+NH_4HCO_3 \rightleftharpoons NaHCO_3+NH_4Cl$. The thermal value of the reaction, $NaCl(96{\cdot}2)+NH_4HCO_3(205{\cdot}6)=NaHCO_3(227{\cdot}0)+NH_4Cl(72{\cdot}7)$, computed from the heats of formation of the four compounds concerned indicated in brackets is $299{\cdot}7-301{\cdot}8=-2{\cdot}1$ Cals. It is probable that ammonium carbonate is formed in the first stage of the operation: $2NH_3+H_2O+CO_2=(NH_4)_2CO_3$; and this reacts with sodium chloride, producing sodium carbonate: $2NaCl+(NH_4)_2CO_3 \rightleftharpoons Na_2CO_3+2NH_4Cl$. Sometimes, indeed, a little sodium carbonate is precipitated before all the ammonia is carbonated, or at any rate a little sodium carbonate is early precipitated, and

that remaining in soln. is further carbonated: $Na_2CO_3+CO_2+H_2O=2NaHCO_3$, and then precipitated. It is thought to be improbable that the ammonia is first converted into ammonium hydrocarbonate, NH_4HCO_3, which then undergoes double decomposition with the sodium chloride, because (*a*) ammonium hydrocarbonate is almost as sparingly soluble as sodium hydrocarbonate in the mother liquids, and would therefore be precipitated; and (*b*) such a reaction would be endothermal, whereas the reaction is really exothermal in agreement with: $CO_2+H_2O+Na_2CO_3=2NaHCO_3+18{\cdot}4$ Cals. The reactions are all reversible, and the proportion of sodium chloride converted into the hydrocarbonate depends upon the relative conc. of the reacting salts.

The reversibility of the reaction was noted by D. Heeren and T. Schlösing,[2] who found that the conversion of sodium chloride into the hydro-carbonate stops with a two-thirds or four-fifths conversion; and J. A. Bradburn was able to reverse the reaction completely by blowing air through the mother liquid containing the sodium hydrocarbonate when the ammonium carbonate formed by the action of ammonium chloride on sodium hydrocarbonate was carried away in a stream of air. An excess of ammonium hydrocarbonate is required to counteract the reversal of the reaction by the action of the ammonium chloride on the sodium hydrocarbonate. E. Solvay stated that he was able to decompose the sodium chloride completely, but he later must have noticed that his yields fell short of this ideal state. H. Schreib found that the proportion of sodium chloride converted into the hydrocarbonate depends on the ratio $NaCl : NH_3$, and on the temp., but is scarcely affected by the press. The basal reaction of the ammonia-soda process can be symbolized:

$$NaCl+NH_4HCO_3 \rightleftharpoons NaHCO_3+NH_4Cl$$

which is a case of what J. H. van't Hoff called a system of reciprocal salt pairs—*der reciproken Salzpolare*. Several methods have been suggested for representing the composition of such systems graphically, by R. Löwenherz, E. Jänecke, R. Kremann, W. Meyerhofer, etc. P. P. Fedotieff expresses his results in the following manner. The solubility of sodium hydrogen carbonate, $NaHCO_3$, per litre of water at 0° is 0·82—this is represented by *OA*, Fig. 63; the solubility of sodium chloride, represented by *OB*, Fig. 63, is 6·09; of ammonium chloride, NH_4Cl, represented by *OC*, Fig. 63, is 5·57; and of ammonium hydrogen carbonate, represented by *OD*, Fig. 63, is 1·52. The points corresponding to sat. soln. of a pair of salts with a common ion—say, sodium and ammonium chlorides—are constructed by marking off the content in $NaHCO_3$ on the *OA* axis, and marking off the content of sodium chloride on the *OB* axis. The point *E* represents soln. sat. with both ammonium hydrogen carbonate and sodium chloride—0·09 and 6·0 respectively; *F*, soln. sat. with sodium and ammonium chlorides, 4·89 and 2·73 respectively; *G*, soln. sat. with ammonium chloride and ammonium hydrogen carbonate, 5·42 and 0·46 respectively; and *H*, soln. sat. with ammonium and sodium hydrogen carbonates, 1·39 and 0·58 respectively. The line *AE* represents the solubility of sodium hydrogen carbonate in the presence of sodium chloride, and *HA*, in the presence of ammonium hydrogen carbonate. The line *EB* represents the solubility of sodium chloride in the presence of sodium hydrogen carbonate, and *BF*, in the presence of ammonium chloride. The line *FC* represents the solubility of ammonium chloride in the presence of sodium chloride, and *CG*, in the presence of ammonium hydrogen carbonate. The line *GD* represents the solubility of

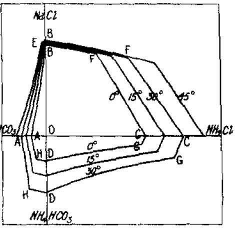


Fig. 63.—Solubility of the Four Salts $NaCl+NH_4HCO_3 \rightleftharpoons NaHCO_3+NH_4Cl$ in Solutions each in presence of another Salt.

ammonium hydrogen carbonate in the presence of ammonium chloride, and DH, in the presence of sodium hydrogen carbonate. J. H. van't Hoff has shown that *for soln. sat. with three salts there are the four possible combinations* :

NaCl, NH_4Cl, NH_4HCO_3 . .	(1)	NaCl, NH_4Cl, $NaHCO_3$ . .	(3)
NaCl, NH_4HCO_3, $NaHCO_3$ . .	(2)	NH_4Cl, NH_4HCO_3, $NaHCO_3$.	(4)

The simultaneous existence of NH_4HCO_3 and of NaCl in (1) or (2), and of the reciprocal system $NaHCO_3$ and NH_4Cl in (3) or (4) is possible only at one definite temp., since if the four salts NaCl, NH_4Cl, NH_4HCO_3, and $NaHCO_3$ could exist in a stable form side by side, they could do so in contact with any soln. that is sat. with them all. Consequently, all four salts of a reciprocal system of salts are possible only at a temp. for which the products of the conc. of the reciprocal pairs are equal, that is, when $C_{NaCl}C_{NH_4HCO_3}=C_{NaHCO_3}C_{NH_4Cl}$. At this temp., the system will be invariant—there are four components, and six phases (4 solids, a liquid, and a vapour). At all other temp. one of the two systems will change into its reciprocal, for the one with the higher conc. product will change into the other. For the system, $NaCl+NH_4HCO_3\rightleftharpoons NH_4Cl+NaHCO_3$, at 0°, 6·09×1·5 is greater than 5·57×0·82. This soln. (3) sat. with NaCl, NH_4Cl, and $NaHCO_3$ would be supersaturated with respect to NH_4HCO_3, so that NaCl and NH_4HCO_3 can never coexist at this temp., but only soln. sat. with :

$$\text{I. } NaHCO_3+NH_4Cl+NH_4HCO_3, \text{ and II. } NaCl+NH_4Cl+NaHCO_3$$

as solid phases are capable of existence. P. P. Fedotieff, *in his Der Ammoniaksodaprozess vom Standpunkte der Phaslenehre*, has made a detailed study of the theory *of the ammonia-soda process. He found that soln. sat. with these combinations* contained :

TABLE XLV.

Solubility.	Soln. I. Solid phase : $NaHCO_3$; NH_4Cl; NH_4HCO_3			Soln. II, $NaHCO_3$; NaCl; NH_4Cl		
	$NaHCO_3$	NaCl	NH_4Cl	$NaHCO_3$	NaCl	NH_4Cl
0°	0·59	0·96	4·92	0·12	4·83	2·74
15°	0·93	0·51	6·28	0·18	4·44	2·98

The isothermal evaporation of a sat. soln. of two salts with a common ion leads *to the separation of both salts, but with sat. soln. of three salts, this may or may* not occur. The isothermal evaporation of solution II furnishes as solid phases the same three salts as are present as solutes. These soln. were called by W. Meyerhofer **congruent solutions,** because, on isothermal evaporation, they furnish as solid phases the same salts as are present as solutes in soln. On the other hand, with solution I the salts which separate as solid phases are different from those present in soln., for sodium chloride appears in place of ammonium hydrocarbonate. In contrast with congruent soln., W. Meyerhofer styled them **incongruent solutions** ; here the sat. soln. contains a different salt from those which are present as solid phases. The gradual addition of sodium chloride to solution I changes the composition of the soln. until the incongruent solution I passes into II ; ammonium hydrocarbonate does not change when added in a similar manner to solution II.

The points P_1 and P_2, Fig. 64, represent soln. sat. with three salts as just indicated, and, when these points are joined with the points corresponding with soln. sat. by two salts with a common ion, the following series of lines is obtained: EP_2 representing soln. sat. with sodium hydrocarbonate and chloride ; P_2F, sodium and ammonium chlorides ; P_1P_2, sodium hydrocarbonate and ammonium chloride ; P_1G, ammonium hydrocarbonate and chloride ; and P_1H, sodium and ammonium

hydrocarbonate. The lines in the resulting diagram form four surfaces corresponding with soln. sat. with one salt in the presence of two others, namely, $HDGP_1$, saturation with ammonium hydrocarbonate; P_1GCFP_2, with ammonium chloride; FP_2EB, with sodium chloride; and $HAEP_2P_1$, with sodium hydrocarbonate. The region $HAEP_2P_1$ is important from the point of view of the ammonia-soda process, for it represents soln. sat. with sodium hydrocarbonate; the curves P_1H soln. sat. with ammonium and sodium hydrocarbonates, and P_1P_2, soln. sat. with sodium hydrocarbonate and ammonium chloride. P_1 represents an incongruent sat. soln., and therefore sodium chloride appears in soln. instead of ammonium hydrocarbonate on the curve P_1H from the point of its intersection with the ammonium chloride axis up to P_1, and similar remarks hold for the curve P_1P_2.

P. P. Fedotieff showed that the change of P_1 with temp. can be represented by the movement of the point H; and this in turn depends on the variation of the solubilities of ammonium hydrocarbonate and chloride. When the temp. approaches 32°, P_1 lies on the ammonium chloride axis, and the incongruent sat. soln. becomes congruent because the same salts now appear in the solid phase as are present in soln.—*viz.*, sodium and ammonium hydrocarbonates and ammonium chloride.

The sodium in the mother liquor remaining after the sodium hydrocarbonate, $NaHCO_3$, has separated out: $NaCl+NH_4HCO_3 \rightleftharpoons NH_4Cl+NaHCO_3$, is conveniently regarded as NaCl, and the ammonia as being distributed between the ammonium hydrocarbonate and the ammonium chloride. P. P. Fedotieff then uses what he calls the *Utilisationskoeffizienten*, and R. Kremann *Ausnutzungskoeffizienten* of the sodium and ammonium in order to discuss the reaction with respect to the consumption—the percentage used up—of brine and of ammonia or ammonium hydrocarbonate Using the chemical symbols in brackets to represent gram-eq. per 1000 grms. of water, and supposing all the chlorine and sodium came into the soln. from the sodium chloride, [Cl]—[Na] represents the sodium which separates out as a solid phase, $NaHCO_3$; and similarly, $[NH_4]-[HCO_3]$ represents the percentage amount of ammonium effectively employed. Consequently, the efficiency coeff., U, of sodium and ammonium are respectively

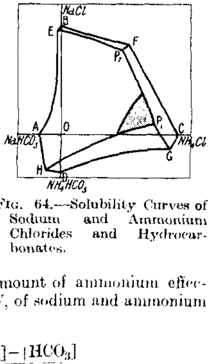


FIG. 64.—Solubility Curves of Sodium and Ammonium Chlorides and Hydrocarbonates.

$$U_{Na}=100\frac{[Cl]-[Na]}{[Cl]};\quad U_{NH_4}=100\frac{[NH_4]-[HCO_3]}{[NH_4]}$$

P. P. Fedotieff gives the data indicated in Table XLVI. The numbers in the NaCl and NH_4HCO_3 columns represent the amounts of these salts employed in the double decomposition in order that, after the solid phase has separated out, soln. may be obtained with the ionic conc. indicated in the next four columns. For convenience, the amount of ammonia in the second part of the NH_4HCO_3 column is expressed in grams.

Soln. on the curve P_2P_1 are sat. with respect to sodium hydrocarbonate and ammonium chloride, and these soln. will be obtained whenever there is a relatively large excess of sodium chloride; and in passing from P_2 to P_1, the ratio $NaCl : NH_3$ (NH_3=unity) changes from 2·19 to 1·69 to 1·31 to 1·08. The greater these ratios—that is, the greater the excess of sodium chloride—the more completely is the ammonia utilized; and the point P_2 corresponds with the utilization of 95·1 per cent. of the available ammonium. On the other hand, the sodium chloride is the more completely utilized, the greater the amount of sodium chloride transformed into sodium hydrocarbonate, and this depends on the amount of ammonium hydrocarbonate;

but this lowers the amount of ammonium hydrocarbonate used up—that is, the more sodium hydrocarbonate remains in soln.

TABLE XLVI.

No.	Salt taken per 1000 grms. of water.		Solutions obtained in gram-equivalents per 1000 grms. of water.				Efficiency coefficient	
	NaCl	NH_4HCO_3/NH_3	HCO_3	Cl	Na	NH_4	U_{Na}	U_{NH_4}
	Solutions on the curve P_1P_2, Fig. 64.							
P_2	479	295/63·4	0·18	8·17	4·62	3·73	43·4	95·1
1	448	360/77·5	0·31	7·65	3·39	4·56	55·7	93·4
2	417	431/92·7	0·51	7·13	2·19	5·45	69·2	90·5
	Solutions on the curve P_1H, Fig. 64.							
P_1	397	496/106·8	0·93	6·79	1·44	6·28	78·8	85·1
3	351	446/ 96·1	0·99	6·00	1·34	5·65	77·7	82·5
4	316	412/ 88·6	1·07	5·41	1·27	5·21	76·4	79·5
5	294	389/ 83·6	1·12	5·03	1·23	4·92	75·5	75·1
6	234	327/ 70·4	1·30	4·00	1·16	4·14	71·0	68·6

The curve P_1H represents soln. sat. with sodium and ammonium hydrocarbonates. The mol. ratio changes only slowly with a considerable difference in the absolute quantities of sodium chloride and ammonium hydrocarbonate to the same quantity of water, namely, starting from P_1, with NH_3=unity, the ratio changes from 1·08 to 1·06 to 1·04 to 1·02, to 0·97. This does not affect the efficiency coeff. of the sodium chloride very much, but it exerts a marked influence on that of the ammonia. Passing along P_1H from P_1, the two efficiency coeff. diminish, and at the point of intersection with the ammonium chloride-axis, when 1·14 mol. of sodium hydrocarbonate and 4·57 mols. of ammonium chloride are present for 1000 grms. of water, the two efficiency coeff. $U_{Na}=U_{NH_4}=75$. An efficiency coeff. of 75 per cent. is obtained by double decomposition with 267 grms. of ammonium chloride and 361 grms. of ammonium hydrocarbonate (77·7 grms. of NH_3). The further course of the curve has no *praktische Bedeutung*.

It will be observed, continues P. P. Fedotieff, that the percentage amount of salt employed which is transformed into hydrocarbonate, U_{Na}, gradually increases *in passing from H to P_2, where it attains a maximum value*; the subsequent decrease in the value of U_{Na} can be followed along the curve P_2E, which represents soln. sat. with *sodium hydrocarbonate and chloride in the presence of variable amounts* of ammonium chloride. Again, the efficiency coeff. of the ammonia, U_{NH_4}, gradually increases from H in passing along the curves HP_1, P_1P_2, and P_2E up to a limiting value of 100 per cent.; but the curve P_2E is of no technical interest. At the temp. of these experiments, 15°, the point P_1 represents the maximum efficiency, U_{Na}, of the sodium chloride; and although the values of U_{Na} change but little on both curves in the vicinity of P_1, the values of U_{NH_4} are very different.

Sodium chloride is so very cheap that it makes very little difference to the cost of the final product whether much or little is utilized; on the other hand, ammonia is comparatively costly, and although that which is not utilized is subsequently recovered, each regeneration is accompanied by losses. It is therefore important for the manufacturer to use up as much ammonia as possible. P. P. Fedotieff considers two soln. with approximately the same U_{Na}, viz. No. 2 (Table XLVI), on the curve P_2P_1, and No. 6, on the P_1H curve. In the former case, after the

deposition of solid sodium hydrocarbonate, 90·5 per cent. of the ammonium hydrocarbonate taken has been utilized, while, in the latter case, only 68·6 per cent. has been utilized. From this point of view, it is advisable to keep on the curve P_1P_2, where the efficiency coeff. of the ammonia are high. This observation is in harmony with empirical experience, and was known to E. Solvay and others. Extremes are odious. If an excess of sodium chloride be employed, some ammonium chloride will be precipitated with the sodium hydrocarbonate, and when such a mixture is calcined some sodium chloride is formed, and the value of the resulting soda ash is accordingly depreciated. It is an interesting exercise to show that if the ammonia were cheap and sodium chloride dear, it would be better to keep near the curve P_1H.

The preceding remarks are based upon observations with soln. sat. with two salts—*viz.* sodium hydrocarbonate and either ammonium chloride or ammonium hydrocarbonate—under manufacturing conditions, however, the soln. are obtained by carbonating ammoniacal soln. sat. with sodium chloride, which are sat. with ammonium hydrocarbonate alone. These soln. are represented by the surface P_1P_2EH. Naturally, many different combinations are here possible, but technical practice is limited to ammoniacal soln. sat. with sodium chloride where the efficiency coeff. U_{NH_4} is not less than 75 per cent. on the P_1P_2-curve. This corresponds with the stippled area in Fig. 64. Obviously, the nearer the working conditions approach P_1P_2 the more complete the utilization of the sodium chloride.

The effect of temp. on the efficiency coeff. for soln. No. 1 (Table XLVI), point P_1, is as follows:

	0°	15°	30°
Efficiency coeff., U_{Na}	73·6	78·8	83·4
Efficiency coeff., U_{NH_4}	88·0	85·1	84·1

This shows that with a rising temp. the yield of sodium hydrocarbonate rises, but the efficiency coeff. of the ammonia decreases. When the temp. exceeds 32°, the amount of sodium chloride in soln No. 1 decreases; at 32°, $U_{Na}=U_{NH_4}$ =84 per cent. There is therefore near 32° an optimum temp. for the yield of sodium hydrocarbonate; in other words, the highest attainable conversion in this reaction is 84 per cent.; or, at 32°, 84 per cent. of the sodium chloride employed is precipitated in the form of sodium hydrogen carbonate. It follows, therefore, that by raising the temp. the efficient area P_1P_2EH is augmented—always supposing that the precipitation and filtration are conducted at one and the same temp.—although in practice this temp. lies near 30°, so that the results of P. P. Fedotieff can be regarded as *Normen für die Praxis*. The condition of equilibrium, at any given temp. is fixed by the equation: $[NaHCO_3][NH_4Cl]=K[NaCl][NH_4HCO_3]$, where the symbols in brackets represent conc. From this equation it would appear that the maximum yield of sodium hydrocarbonate is favoured by high conc. of the sodium chloride and ammonium hydrocarbonate; the latter condition is favoured by a high conc. of ammonia and carbon dioxide.

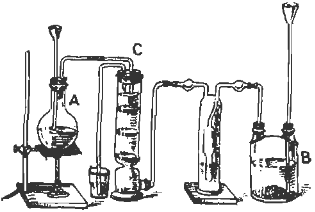


FIG. 65.—Illustration of Solvay's Process.

This process can be illustrated by connecting an apparatus, *A*, for generating ammonia, Fig. 65, and an apparatus, *B*, for making washed carbon dioxide with a tower, *C*, filled with a sat. soln. of sodium chloride and fitted with four perforated iron discs as shown in the diagram. The tower is provided with an exit tube dipping in a beaker of water. The soln. is first sat. with ammonia, and then with carbon dioxide. In about an hour, crystals of sodium bicarbonate will be deposited on the perforated shelves.

The brine is first sat. with ammonia by running downwards through a tower fitted with several compartments, as indicated in Fig. 66, and the ammonia rising upwards bubbles through the liquid in each compartment. A similar tower is employed for recovering the ammonia subsequently carried away during the carbonating of the ammoniated brine. The ammoniated brine is cooled to 30° and, in E. Solvay's apparatus, is pumped to the top of a tower, Fig. 67, 70 to 90 ft. high, and 5 to 7 ft. diameter. The ammoniated brine falls over a series of baffle plates and during its descent meets an ascending stream of carbon dioxide. Some heat is evolved during the absorption of the carbon dioxide, and accordingly W. B. Cogswell (1887) fitted the tower with coolers consisting of a number of mild steel tubes expanded into a steel tube plate. The cold water running through these tubes cools the liquor as it approaches the bottom of the tower. Crusts of salt gradually form on the tower, these have to be removed from time to time, either by a jet of steam or by a stream of fresh brine. The carbonating may be conducted in two stages—in one tower the ammonia is converted approximately to the normal carbonate, and in a second tower the hydrocarbonate is formed. Many other carbonating towers have been devised—*e.g.* in M. Honigmann's the carbon dioxide is purified in series through the ammoniated brine contained in three or more conical vessels fitted with cooling pipes. The liquor which runs from the carbonating tower is filtered through flannel fitted upon rotating cylinders inside of which a vacuum is maintained. The layer of sodium hydrocarbonate is washed with water as the cylinder rotates, and is then automatically scraped off with a knife. W. Mason's analysis (1914) of the soln. when precipitation begins shows that 50 per cent. of the sodium chloride has decomposed and 11·8 per cent. of sodium carbonate is in soln. The mother liquid remaining after the precipitation of the sodium hydrocarbonate contains in grams per 100 c.c. :

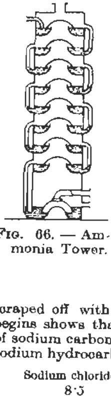


FIG. 66. — Ammonia Tower.

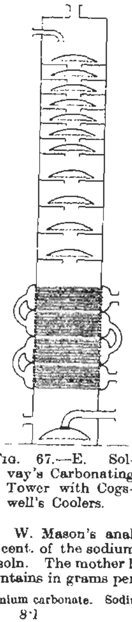


FIG. 67.—E. Solvay's Carbonating Tower with Cogswell's Coolers.

Sodium chloride.	Ammonium carbonate.	Sodium carbonate.	Ammonium chloride.
8·5	8·1	0·5	78·1 per cent.

while the precipitate contains :

Sodium chloride.	Sodium hydrocarbonate.	Sodium carbonate.	Ammonia.	Moisture.
0·2	71·3	4·0	0·5	24·0 per cent.

The ammonia is retained very tenaciously by the crystals and cannot be removed by washing. The mother liquor contains about 90–92 per cent. of the ammonia originally present in the ammoniated brine ; about 8 per cent. will have been carried off by the current of carbon dioxide in Solvay's tower, and is recovered as previously indicated.

If sodium carbonate is needed, the hydrocarbonate is calcined : $2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$.

The sodium hydrocarbonate is heated to drive off the moisture and ammonia, and subsequently to a higher temp. in a Thelen's pan which consists of cast-iron semicircular plates, 6 to 10 ft. in diameter and 7 to 8 ft. long, clamped together end to end in suitable flanges so as to make a length of 30 to 50 ft. The hydrocarbonate is fed mechanically into the furnace and carried backwards and forwards by a number of scrapers attached to a rotating shaft, and ultimately discharged at the opposite end to the feeder. The pans are heated externally longitudinally along the furnace.

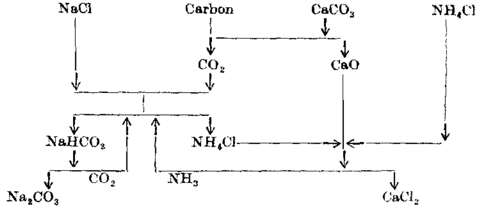
The carbon dioxide given off during the calcination forms part of that used in the first stage of the operation. The mother liquid remaining after the separation

of sodium hydrocarbonate is treated with lime obtained by burning limestone: $CaCO_3=CaO+CO_2$; and the ammonia is recovered: $2NH_4Cl+CaO=CaCl_2+H_2O+2NH_3$. The ammonia and carbon dioxide evolved in these two operations are used again. Thus calcium chloride is the only by-product which is not utilized. G. Bodländer and P. Breull enumerate the three main reactions as: $NaCl+NH_3+CO_2+H_2O=NaHCO_3+NH_4Cl$; $CaCO_3=CaO+CO_2$; and $CaO+2NH_4Cl=CaCl_2+2NH_3+H_2O$, which are summarized into $2NaCl+CaCO_3+CO_2+H_2O=2NaHCO_3+CaCl_2$. The heat balance is therefore:

TABLE XLVII.

Heat consumed.		Heat produced.	
$CaCl_2$ in soln. . .	187·2 Cals.	2NaCl solid . .	195·2 Cals.
$2NaHCO_3$ solid . .	459·8 Cals.	CO_2 gas . . .	97·0 Cals.
		$CaCO_3$ solid . .	270·4 Cals.
		H_2O liquid . .	68·4 Cals.
Total . . .	647·0 Cals.	Total . . .	631·0 Cals.

Consequently, 647−631=16 Cals. are used up in the inverse reaction, the same quantity is absorbed by the technical process, which is therefore possible only by supplying energy from without the system. The following is a schematic representation of the ammonia-soda process:



Several modifications of E. Solvay's process have been proposed. For example, in T. Schlösing's process, solid ammonium hydrocarbonate was used. E. Dresel and J. Lennhof[3] mixed sodium chloride with neutral ammonium carbonate, or sulphite, or borate, and precipitated the sodium salt—carbonate, sulphite, or borate—by passing ammonia either under press. or into a well-cooled soln. G. Claude[4] recommended using synthetic ammonia in the Solvay process, so as to obtain ammonium chloride to be used as a fertilizer; there is no waste calcium chloride since the chlorine of the sodium chloride forms ammonium chloride. In H. A. Frasch's process, nickel or cobalt oxide, hydroxide, or carbonate is allowed to act on approximately its eq. of alkaline chloride in the presence of ammonia; and insoluble nickel hexamminochloride, $Ni(NH_3)_6Cl_2$, is formed: $Ni(OH)_2+6NH_3+2NaCl=Ni(NH_3)_6Cl_2+2NaOH$. When the double nickel salt is treated with milk of lime, nickel hydroxide is regenerated, and the ammonia can be recovered from ammonium chloride which is formed. The carbonates can be used in place of the oxides; and potassium chloride in place of the sodium salt. M. Bernard used methylamine, and J. Ortlieb and J. A. Müller, trimethylamine, in place of ammonia for preparing potassium carbonate; and H. de Grousilliers used alcoholic in place of aq. soln. J. Bower (1840) patented the use of sodium sulphate in place of sodium chloride in the ammonia-soda process. G. T. Gerlach, H. Gaskell and F. Hurter, G. Blattner, F. Hurter and J. Omholt, and C. Wigg, also worked on this

process. In 1876, G. T. Gerlach (1876) and J. F. Chance (1885) proposed the use *of sodium nitrate in place of sodium chloride in the ammonia-soda process.* Sodium hydrocarbonate and ammonium nitrate are formed : $NaNO_3+NH_4HCO_3+NaHCO_3+NH_4NO_3$. The yield of ammonium nitrate is 87·5 per cent. of the theoretical, and J. A. Colson recommends this process as being more favourable than the ordinary E. Solvay's process. The residual sodium and calcium nitrates can be utilized as manures. E. W. Parnell and J. Simpson patented a combination of the Leblanc and ammonia-soda processes by decomposing the ammonium chloride produced in the latter by the calcium sulphide produced in the former : $2NH_4Cl+CaS=CaCl_2+(NH_4)_2S$. The latter escapes as vapour and is absorbed in water. The cold soln. is treated with carbon dioxide : $(NH_4)_2S+2CO_2+2H_2O=2NH_4HCO_3+H_2S$. The ammonium hydrocarbonate is treated with sodium chloride as in the ordinary process.

Potassium carbonate cannot be made economically by Solvay's process because the potassium hydrocarbonate is too soluble ; but if trimethylamine be used in place of using ammonia, J. Ortlieb and J. A. Müller have shown that potassium hydrocarbonate will be precipitated.[5] A great deal of the potassium carbonate of commerce is made by N. Leblanc's process.

The Leblanc process has had to meet severe competition with the ammonia-soda and the electrolytic process. It is probable that if it had not been for the sulphur recovery processes it would have been entirely defunct long ago, this not only on account of the losses of sulphur, but on account of the objectionable nature of the alkali waste. The Leblanc process, however, is generally regarded as a declining industry, although it still holds its own. The prop which keeps the Leblanc process from falling into oblivion is the by-product chlorine which can be sold at a good price in the form of hydrochloric acid or bleaching powder. The struggle of the Leblanc process for existence is well shown by the following table, which gives the output of soda by the different processes expressed in tons per annum :

TABLE XLVIII.

	1865	1875	1885	1895	1905	1911
Leblanc	350,000	490,000	440,000	270,000	140,000	130,000
Ammonia-soda	—	30,000	320,000	980,000	1,700,000	1,900,000
Electrolytic	—	—	—	—	10,000	50,000
Total	350,000	520,000	760,000	1,250,000	1,850,000	2,080,000

The production of caustic soda has largely replaced that of carbonate by the Leblanc process, although the electrolytic process is a serious competitor in this field.

The *sodium chloride and sulphate regularly found in Leblanc soda ash* are not usually injurious ; the insoluble matter should not exceed 1 to $1\frac{1}{4}$ per cent. It consists principally of calcium carbonate, alumina, silica, and ferric oxide. The sulphides should not be detectable by lead paper ; thiosulphates are destroyed in calcining the ash ; sulphites are usually present and can be detected by iodine soln. ; and sodium hydroxide, except in the so-called caustic ash, does not usually exceed 1 per cent. The moisture in fresh ash ranges below one per cent. Owing to the mode of preparation, ash by Solvay's process is more pure than that prepared by Leblanc's process. It does not contain sodium hydroxide, sulphides, sulphites, or thiosulphates ; it may contain a slight excess *of carbon dioxide ; a little sodium sulphate is always present ; iron, alumina,* and silica are present in minute traces ; sodium chloride is perhaps the only

impurity of note. The following are analyses of soda ash by Leblanc's and Solvay's processes:

	Na_2CO_3	NaOH	NaCl	Na_2SO_4	SiO_2	$Fe_2O+Al_2O_3$	MgO	$CaCO_3$	Water
Leblanc ash .	96·7	0·1	0·3	0·9	1·0	0·4	0·1	—	0·7
Solvay ash .	98·8	—	0·4	0·2	0·09	0·02	0·1	0·04	0·35

Salt-cake is used in the soda pulp and in the glass industries, and the demand has at times been greater than can be supplied by the salt-cake as a by-product in the manufacture of hydrochloric acid. As a result, the deposits of Glauber's salts or mirabilite near the Downey Lakes (Laramie, Wyoming), Carrizo Plains (San Louis, Obispo County, Cal.), etc., have been exploited.

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§ 31. The Properties of the Alkali Carbonates

Anhydrous lithium carbonate forms a voluminous white powder; both A. Arfvedson[1] and L. Kralowansky obtained the salt in a **crystalline form**, and by evaporating a soln. sat. at 15°, F. C. Flückiger obtained long prisms which, according to E. Mallard, belong to the monoclinic system, with axial ratios $a:b:c=1{\cdot}672:1:1{\cdot}244$, and $\beta=114°\ 25'$. The fused salt also furnishes a mass

of crystals on cooling. Anhydrous sodium potassium, rubidium, and cæsium carbonates are white solids whose crystalline forms have not yet been determined.

The **specific gravity** of lithium carbonate, according to P. Kremers, is 2·111 (17·5°); according to G. Quincke, 2·111 (0°); and, according to E. Mallard, 2·094. G. Quincke also found the sp. gr. of lithium carbonate at the m.p. to be 1·787, while E. Brunner found this constant to be $1·765-0·00034(\theta-900)$ at a temp. $\theta°$, between 800° and 1000°. The values for the sp. gr. of sodium carbonate range from P. A. Favre and C. A. Valson's 2·407 (20·5°), to L. Playfair and J. P. Joule's 2·430, to G. J. B. Karsten's 2·4659, to H. G. F. Schröder's 2·500, to E. Filhol's 2·509, and to C. Quincke's 2·509 (0°), F. Braun found 2·041 at 900°, G. Quincke 2·041 at the m.p., and E. Brunner $1·9445-0·0040(\theta-900)$ at $\theta°$ between 800° and 900°. The sp. gr. of potassium carbonate was found to be 2·103 by L. Playfair and J. P. Joule; 2·105 by W. C. Smith; 2·2643 by C. J. B. Karsten; 2·267 by E. Filhol; and 2·29 by H. G. F. Schröder. G. Quincke gives for the sp. gr. at 0° 2·3, and at the m.p. 2·2; while F. Braun gives 2·00 as the value of this constant at the m.p. E. Brunner represented the sp. gr. of lithium carbonate, $D=1·765-0·00034(\theta-900)$; sodium carbonate, $D=1·9445-0·00040(\theta-900)$; and potassium carbonate at $\theta°$ between 800° and 1000° by $1·900-0·00046(\theta-900)$. The sp. gr. of rubidium and cæsium carbonates have not been determined. G. Quincke also gives the **surface tension** of the molten lithium carbonate as 152·5 dynes per cm.; molten sodium carbonate as 179·0 dynes per cm.; and of molten potassium carbonate, 160·2 dynes per cm. The corresponding values for the **specific cohesion** are respectively $a^2=17·39$, 17·88, and 16·33 sq. mm. G. Wertheim measured the **velocity of sound** in soln. of sodium carbonate.

According to H. V. Regnault,[2] the **specific heat** of sodium carbonate previously fused is 0·2728 between 16° and 98°, and H. Kopp 0·246 between 18° and 48°. For potassium carbonate H. V. Regnault found 0·21623 between 23° and 29°, and H. Kopp, 0·200 between 17° and 47°—that is, 29·81 and 28·43 respectively per mol. H. Kopp also found the sp. ht. of rubidium carbonate to be 0·123 between 18° and 47°. According to A. Arfvedson, lithium carbonate melts at a dark red heat, and, according to F. C. Flückiger, it melts more readily than either sodium or potassium carbonate, forming, according to R. Hermann, a viscous fluid, which freezes to a crystalline mass. W. Ramsay and N. Eumorfopoulos give 618° for the **melting point** of lithium carbonate; T. Carnelley gave 699°±4° in 1876, and 695±4° in 1878; H. le Chatelier gives 710° for the m.p., and K. Hüttner and G. Tammann give 734·5° for the f.p. H. le Chatelier observed the f.p. curve of mixtures of lithium and sodium carbonates has a eutectic at about 690° with mixtures containing 48·5 per cent. of sodium carbonate; with lithium and potassium carbonates, there is a eutectic at 500° with about 26 per cent. of lithium carbonate; a maximum at 515° corresponding with **potassium lithium carbonate,** $LiKCO_3$; and a second eutectic at 492° corresponding with 46·6 per cent. of lithium carbonate. According to K. Hüttner and G. Tammann, there is a break in the heating curve of sodium carbonate near 450°, showing that it here undergoes a transformation into another form, and they estimate the heat of the transformation to be $\frac{1}{22}$ of the heat of fusion; O. Sackur gives approximately 4 cals. per gram. According to A. Jacquelain, sodium carbonate melts more readily than the potassium salt. The m.p. of sodium carbonate is 849·0°, according to V. Meyer and W. Riddle; 850° to 867·3°, J. McCrae; 852°, C. T. Heycock and F. H. Neville; 851°, W. Ramsay and N. Eumorfopoulos; 852°, K. Arndt; and 853°, K. Hüttner and G. Tammann. According to H. le Chatelier, the m.p. of sodium carbonate is lowered 200° when mixed with 34·7 per cent. of sodium chloride; 130° by 51·5 per cent. of potassium carbonate; and 30° by 39·8 per cent. of sodium sulphate. O. Sackur has also measured the effect of additions of about 10 per cent. of sodium or potassium chloride, on the f.p. of sodium carbonate. According to P. Niggli, the binary system sodium chloride and carbonate has a eutectic at 640°. According to K. Hüttner and G. Tammann, there is a break in the heating curve of potassium

carbonate at about 410°, analogous to the break at 450° with sodium carbonate. V. Meyer and W. Riddle found the m.p. of potassium carbonate to be 878·6°; H. le Chatelier, 885°; J. McCrae, 888·9°; W. Ramsay and N. Eumorfopoulos, 880°; K. Hüttner and G. Tammann, 894°; and K. Arndt, 900°. According to P. Niggli, potassium and sodium carbonates form a continuous series of mixed crystals with a minimum point on the curve at about 712° with about 46 mols. per cent. of potassium carbonate. According to R. Bunsen, rubidium carbonate melts at a red heat, and T. Carnelley and W. C. Williams place the m.p. at 837°. O. Sackur calculated the **heat of fusion** of sodium carbonate to be 82 cals. per gram; and potassium carbonate, 66 cals. per gram. The **molecular lowering of the freezing point** of potassium carbonate as a solvent is 41°, and of sodium carbonate, 31°. O. Sackur studied soln. of potassium chloride, sodium chloride, and potassium or sodium manganate in fused alkali carbonates.

The volatility of lithium carbonate was studied by R. Bunsen: he found that this compound volatilizes in the hottest part of a Bunsen flame 8·74 (and by T. H. Norton and D. M. Roth 10) times as rapidly when melted as the same quantity of sodium chloride. According to L. Troost, lithium carbonate begins to decompose before it melts, and when melted it loses carbon dioxide, rapidly at first, but more slowly later on, until but 17 per cent. of the total remains, and P. Lebeau found that when heated in vacuo, all the carbon dioxide can be driven off, and a part of the resulting oxide is volatilized. P. Lebeau found the **dissociation pressure** of lithium carbonate to be at:

	580°	610°	620°	740°	840°	930°	1000°	1200°
Press. . .	0	1	3	19	37	61	91	300 mm.

J. Johnston also measured the dissociation press. of lithium carbonate, and estimates that it is about an atm. at 1270°. W. Dittmar found that lithium carbonate is converted into the oxide when heated in a stream of hydrogen.

Sodium carbonate was found by R. Bunsen to volatilize in the hottest part of a bunsen flame 7·50 (and by T. H. Norton and D. M. Roth 7·38) times as rapidly as the same quantity of sodium chloride. W. Dittmar investigated the behaviour of sodium carbonate on ignition with a view of using this salt as a standard for preparing normal soln. of acid; he found that this salt is not changed by heating it to redness in an atmosphere of carbon dioxide, but in nitrogen or in hydrogen, it respectively decomposes into oxide and hydroxide. J. L. Gay Lussac and L. J. Thénard, and M. Jacquelain found that if melted in a platinum vessel, steam will drive out carbon dioxide in consequence of the formation of sodium hydroxide. According to P. Lebeau, sodium carbonate dissociates when heated to a high temp. in vacuo; and some is volatilized; the dissociation press. is:

	700°	880°	990°	1010°	1100°	1150°	1180°	1200°
Press. . .	1	10	12	14	21	28	38	41 mm.

J. Johnston also measured the dissociation press. of this salt and found it to be an atm. at 1500°. T. Scheerer noted that sodium carbonate lost 1·34 to 1·38 per cent. in weight when heated to yellow heat (*c.* 1000°), and about half per cent. at a red heat. E. Mallard found that when heated in a blast flame, sodium carbonate did not lose more than 1·75 per cent. in weight if the crucible be in the carbon dioxide zone of the flame; but if air free from carbon dioxide be simultaneously passed through the crucible, the loss is proportional to the time—about 1·5 mgrm. per minute. According to R. Kissling, a loss of carbon dioxide can be detected when sodium carbonate is heated to 400°, and, according to R. Hefelmann, the loss is not recuperated completely on cooling. Purified sodium carbonate fused in an atm. of carbon dioxide is a glass which is not very hygroscopic and is very suitable as a standard for preparing soln. for volumetric analysis. When heated in platinum crucibles over a gas blowpipe flame, the diffusion of some hydrogen through the

platinum walls may decompose a minute quantity of carbonate, as was shown by S. U. Pickering.

Potassium carbonate was also found by R. Bunsen to volatilize 3·23, and by T. H. Norton and D. M. Roth 3·61 times as fast as the same quantity of sodium chloride under similar conditions. P. Leblanc found that it can be completely volatilized in vacuo and that its dissociation press. is :

	730°	790°	810°	890°	960°	970°	1000°	1090°
Press. . .	0	0·5	1	3	5	9	12	17 mm.

T. Scheerer found that when heated to a yellow heat (c.1000°), in a closed platinum crucible, potassium carbonate loses about 0·5 per cent. in weight owing to the loss of carbon dioxide which is taken up again at lower temp. W. Dittmar could detect no change when heated to redness in an atm. of carbon dioxide, but it is partially converted into oxide in an atm. of nitrogen, and still more so in an atm. of hydrogen. P. Lebeau found that rubidium and cæsium carbonates lose carbon dioxide when heated in vacuo, and, if the vacuum be maintained, decomposition is complete. P. Lebeau also found that the dissociation press. of rubidium carbonate is :

	690°	740°	830°	870°	900°	990°	1020°	1080°
Press. . .	0	2	6	8	10	18	20	33 mm.

and the dissociation press. of cæsium carbonate :

	610°	630°	680°	830°	1000°	1130°	1150°	1180°
Press. . .	2	4	8	32	44	121	137	157 mm.

D. D. Jackson and J. J. Morgan found the **vapour pressure** of the oxide derived from potassium carbonate to be 1·68 mm. of mercury at 970°, and 5·0 mm. at 1130°.

According to W. E. Müller,[3] the **heat of formation** : $2LiOH_{aq}+CO_{2aq}=Li_2CO_{3aq}+20{\cdot}4$ Cals., and for (Li_2O, CO_2) R. de Forcrand gives 54·23 Cals. N. N. Beketoff gave for (Na_2O, CO_2). 75·92 Cals., R. de Forcrand, 76·88 Cals. ; and J. Thomsen, 75·92 Cals. ; for (Na_2, O_2, CO_2), 243·64 Cals. ; and for (2Na, C, 3O), 272·64—M. Berthelot, 270·8 Cals. ; and R. de Forcrand, 271·97 Cals. J. Thomsen also gives for (2Na, 2O, CO, $10H_2O$), 265·44 Cals. ; for $2NaOH+CO_2=Na_2CO_3.H_2O+43{\cdot}69$ Cals. ; $2Na_2O_{aq}+CO_{2aq}=20{\cdot}18$ Cals. ; $2Na_2O+2CO_2=22{\cdot}03$ Cals. ; and for $2Na_2O+0{\cdot}5CO_2=10{\cdot}30$ Cals. M. Berthelot found $2KOH_{aq}+CO_{2aq}=20{\cdot}2$ Cals. R. de Forcrand gives for (K_2O, CO_2), 92·46 Cals. J. Thomsen gives for (2K, C, 3O) 281·1 Cals. ; M. Berthelot, 278·8 Cals. ; and R. de Forcrand, 275·37 Cals. R. de Forcrand gives for (2Rb, C, 3O), 274·9 Cals. ; for ($Rb_2O_2CO_2$), 97·47 Cals. ; *for (2Cs, C, 3O), 274·54 Cals. ; and for Cs_2O, CO_2), 97·53 Cals. It will be observed* that R. de Forcrand's values for the heats of formation of the normal carbonates of potassium, rubidium, and cæsium decrease with increasing at. wt. of these elements—*viz.* 275·37, 274·9, and 274·54 Cals.—a result which *a priori* appears highly improbable. He also gives for $2RbOH_{aq}+CO_{2aq}=20{\cdot}57$ Cals. ; and for $2CsOH_{aq}+CO_{2aq}=20{\cdot}57$ Cals. According to J. Thomsen, the **heat of hydration** for the first molecule of water by anhydrous sodium carbonate is 3·382 Cals. ; for the second, 2·234 Cals. ; for the third and fourth, about 2·109 Cals. The heat of formation of the monohydrated carbonate from the anhydrous salt : $Na_2CO_3+H_2O_{liquid}=Na_2CO_3.H_2O+3{\cdot}382$ Cals. ; for $Na_2CO_3.H_2O+6H_2O_{liquid}=Na_2CO_3.7H_2O+13{\cdot}02$ Cals. ; and for $Na_2CO_3.7H_2O+3H_2O_{liquid}=Na_2CO_3.10H_2O+5{\cdot}394$ Cals. J. Thomsen gave 21·8 Cals. for the heat of formation of the decahydrated carbonate from the anhydrous salt ; and P. A. Favre and C. A. Valson, 23·0 Cals.

According to M. Berthelot and L. Ilosvay de Nagy Ilosva, the **heat of solution** of anhydrous sodium carbonate is 5·64 Cals. ; of $Na_2CO_3.H_2O$, 2·25 Cals. ; of $Na_2CO_3.2H_2O$, 0·02 Cals. ; and of $Na_2CO_3.10H_2O$, $-16{\cdot}16$ Cals. ; the heat of soln. of anhydrous sodium carbonate at $\theta°$ is $2{\cdot}810+0{\cdot}022(\theta-0{\cdot}015)$ Cals. M. Berthelot in his study : ***Les sels doubles préparés par fusion,*** found that sodium carbonate after fusion dissolves in water with a greater evolution of heat than it does before

fusion, and suggested that the salt exists in two modifications with different heats of soln. in water. S. U. Pickering, however, showed that the excess of heat with the fused salt is due to a certain fraction of the carbonate having been decomposed during the process of fusion—*vide supra*. According to J. Thomsen, the heat of soln. of anhydrous potassium carbonate is 6·49 Cals., and, according to M. Berthelot, 6·54 Cals. The heat of soln. of anhydrous potassium carbonate at $\theta°$ is, according to M. Berthelot and L. Ilosvay de Nagy Ilosva, $6·50+0·074(\theta-15)$ Cals. According to M. Berthelot, at 17·6°, crystallized hydrated potassium carbonate dissolves with the absorption of heat, furnishing −0·122 Cal. at 32°, and also, according to L. C. de Coppet, at 100°, with the evolution of heat, *e.g.* +0·120 Cal.; at 25°, heat is neither absorbed nor evolved. According to J. Thomsen, the heat of soln. of potassium carbonate, $K_2CO_3.1\frac{1}{2}H_2O$, is −0·38 Cals., and of the partly dehydrated potassium carbonate of the composition $K_2CO_3+\frac{1}{2}H_2O$, 4·28 Cals. According to M. Berthelot, the heat of formation, $K_2CO_3+1\frac{1}{2}H_2O_{liquid}=6·88$ Cals. R. de Forcrand gives for the heat of soln. of rubidium carbonate, 8·75 Cals., and for cæsium carbonate, 11·84 Cals. N. Galitzky measured the heat of soln. of potassium carbonate in mixtures of alcohol and water, and noted that less heat is evolved than is the case with water alone; the maximum occurs with 50 parts of alcohol for 100 of water.

J. Thomsen found the **heat of dilution** of $Na_2CO_3+30H_2O$ with 50 mols. of water, −0·556 Cals.; with 100 mols. of water, −1·190 Cals.; and with 200 mols., 1·601 Cals. W. A. Tilden gives for the heat of soln. of a mol. of sodium carbonate in 100 mols. of water at 22°, 6·322 Cals.; at 35°–40°, 6·842 Cals.; at 40°–45°, 6·768 Cals.; and at 50°–55°, 6·958 Cals. P. A. Favre also reported that a soln. of potassium carbonate sat. at 24°, develops much heat when diluted with water. The heat of dilution of potassium carbonate amounts to −0·10 to −0·70 Cal. The difference in the heat of soln. of potassium carbonate soln. of different conc. indicates that hydrates are present in the more conc. soln. and that their heat of formation is positive, and heat of soln. negative.

The hydrates of lithium carbonate have not been investigated, but quite a number of hydrated forms of sodium carbonate with 1, 2, 2½, 3, 5, 6, 7, 8, 9, 10, and $15H_2O$ have been reported, though the majority of these are probably mixtures or intermediate stages in the passage from a higher to a lower form. The first of these occurs as *thermonatrite*, $Na_2CO_3.H_2O$, or **monohydrated sodium carbonate** effloresces in Hungary; as an incrustation on the lava from Vesuvius; the soda deposits in Egypt; near the coast at Aden; near Ararat; Borku (Africa); and as a soil efflorescence at San Joaquintal (California). According to W. Haidinger's analysis,[4] the formula is $Na_2CO_3.1\frac{1}{2}H_2O$, but R. Schindler's and H. Löwel's work showed that the formula is more correctly $Na_2CO_3.H_2O$. Attempts have been made to show that this compound is the disodium salt of orthocarbonic acid, $C(OH)_2$, namely, $(OH)_2C(ONa)_2$, although, of course, it is not known how the water is associated in the molecule.

H. Löwel obtained monohydrated sodium carbonate as a crystalline crust by boiling aq. soln. of sodium carbonate. According to W. Haidinger, this salt crystallizes from aq. soln. of sodium carbonate between 25° and 37°; R. Schindler said 75°; and J. C. G. de Marignac gave 80°. As indicated in Fig. 68, monohydrated sodium carbonate is the stable solid phase, in the presence of aq. soln. at a temp. exceeding 32·5°—the transition point for the transformation of decahydrated sodium carbonate to the heptahydrated carbonate: $Na_2CO_3.7H_2O \rightleftharpoons Na_2CO_3.H_2O+6H_2O$. According to J. C. G. de Marignac, the transition point is lowered by the presence of salts like sodium chloride, or potassium carbonate, and this fact may account for W. Haidinger having obtained the salt at temp. below the normal transition point. According to W. Haidinger, the monohydrated salt is formed when the decahydrated salt is melted in its own water of crystallization; and, according to R. Schindler, it is also formed when one of the higher hydrates is kept at a temp. between 32·5° and 37·5°. The crystals of monohydrated sodium carbonate,

$Na_2CO_3.H_2O$, form bipyramidal crystals belonging to the rhombic system, with, according to J. C. G. de Marignac, the axial ratios $a:b:c=0.8268:1:0.4044$. The sp. gr. of the natural salt, thermonatrite, is given as 1·5 to 1·6 ; and the hardness as 1·0 to 1·5. According to W. Haidinger, it does not melt when heated, but loses its combined water between 87° and 100°—G. J. Mulder gives 73°—and forms a pulverulent mass. The curve in Fig. 68 shows that the monohydrated salt is less soluble in water to, say, 104° than it is at the lower temp. 38°, so that, as H. Löwel pointed out, on heating a sat. soln. of the salt crystals of the monohydrated salt separate as the temp. rises, and redissolve as the soln. cools. According to R. Schindler, the monohydrated salt in dry weather at 12·5° absorbs enough water from the air to raise the percentage amount of contained water from 14·5 to 46·0, and in moist air it absorbs still more ; it also absorbs some carbon dioxide from the air, forming the sesqui-carbonate. H. Lescœur has measured the vap. press. p of sodium monohydrated carbonate, and R. M. Caven and H. J. S. Sand found it to be 7·9 mm. at 30·5° ; 93·2 mm. at 66·4° ; and 539·1 mm. at 97·7°, and they represent a whole series of observations by the formula $\log p=a-b/T$, where T represents the absolute temp. and a and b are constants respectively 10·825 and 3000·0. Since the heat of the reaction Q is related with the constant b, by $Q=\log 10Rb$, where R denotes the gas constant, 2 cals. per mol. per degree, the heat of dissociation of a mol. of monohydrated sodium carbonate is 13,800 cals.

In preparing sodium monohydrated carbonate, the wet crystals may combine with the adherent mother liquor, forming the decahydrated salt, and this accounts for the high results usually obtained in determinations of the amount of water in the crystals ; and it possibly explains how a number of other hydrated salts have been reported at different times. The evidence of the individuality of the crystals of sodium carbonate with 2, $2\frac{1}{2}$, 3, 5, or $6H_2O$ is quite inadequate.

J. Thomsen [5] reported that *dihydrated sodium carbonate*, $Na_2CO_3.2H_2O$, separates from the hot liquid obtained by melting the decahydrated carbonate. W. Haidinger says the monohydrated salt is formed under these conditions. According to A. Morel, *hemi-pentahydrated sodium carbonate*, $Na_2CO_3.2\frac{1}{2}H_2O$, crystallizes in needle-like crystals from conc. soln. of Solvay soda between 18° and 25° ; and by evaporating below 25° a mixed soln. of sodium carbonate in sodium phosphate. He adds that the crystals do not change very much when kept in their own mother liquid between 0° and 40°, and that the rhombic prisms have the axial ratios $a:b:c=0.794:1:0.439$. F. Schickendantz reported *trihydrated sodium carbonate*, $Na_2CO_3.3H_2O$, to be associated with the efflorescent soda in the dried river beds of the Cordilleras. R. Schindler says that the weathering of the crystals of decahydrated sodium carbonate in dry air at 12·5° furnishes crystals of *pentahydrated sodium carbonate*, $Na_2CO_3.5H_2O$; J. J. Berzelius also says that these crystals are formed at 33° by melting the decahydrated salt and pouring off the clear liquid. J. F. Persoz added that the crystals are rhombic octahedra which crystallize unchanged from water at about 30°. E. Mitscherlich reported the formation of crystals of *hexahydrated sodium carbonate*, $Na_2CO_3.6H_2O$, when soln. of sodium sulphide are exposed to air, and form an aq. soln. of sodium carbonate and sodium chloride.

T. Thomson [6] discovered that crystals of **heptahydrated sodium carbonate**, $Na_2CO_3.7H_2O$, were formed during the cooling of the liquid obtained by heating the decahydrated carbonate up to its m.p., or by cooling a hot sat. aq. soln. at a temp. lower than that at which crystals of the monohydrated carbonate are formed, and higher than that at which the decahydrated carbonate is formed. The range of stability is indicated in Fig. 68. C. F. Rammelsberg also obtained the heptahydrated carbonate by cooling the melted decahydrated carbonate. C. F. Rammelsberg also considered that W. Haidinger's crystals of the monohydrated carbonate are really the heptahydrated salt because the analysis by W. Haidinger showed the presence of 17·74 per cent. instead of 14·47 per cent. of water required for the monohydrated salt. R. Schindler attributed the large proportion of water in W. Haidinger's crystals to their having been but imperfectly freed from the mother liquor by drying at 37·5° between filter paper. J. C. G. de Marignac occasionally obtained crystals from soln. containing sodium iodate, and he specially remarked on *la beauté des cristaux* which separated from

soln. containing sodium chloride or nitrate in addition to the sodium carbonate. H. Löwel also emphasized the importance of preventing access of air to the soln. from which the heptahydrated carbonate is to be obtained—possibly because atm. dust contains some sodium decahydrated carbonate dust, which inoculates the solution with the wrong nuclei. H. Löwel also noted that there are dimorphic forms of the crystals—rhombohedral and rhombic—with different solubilities in water.

The clear transparent rhombohedral crystals of α-$Na_2CO_3.7H_2O$ are unstable and readily pass into the rhombic bipyramidal crystals of β-$Na_2CO_3.7H_2O$. The crystals of the α-salt soon become milk-white owing to the formation of the decahydrated salt by the re-crystallization of the heptahydrated carbonate moist with the adherent water. The solubility curve is indicated in Fig. 68. H. Löwel prepared the unstable rhombohedral or α-salt in the following manner:

Half fill a flask with a sat. aq. soln. of sodium carbonate, and boil the liquid for 15–20 minutes until a little monohydrated carbonate is formed. Close the flask with a cork, fitted with two glass tubes, and keep the temp. at 10°–15° till some crystals are formed. Run in alcohol of sp. gr. 0·835 and temp. of 45° until the flask is full. Crystals of the α-salt are formed after standing four or five days at a temp. of 16·22°. The crystals are isolated, by drawing on the mother liquid, and adding alcohol before the mother liquor is quite gone. The remaining mother liquor is then drawn off.

The crystals of heptahydrated sodium carbonate prepared by T. Thomson, J. C. G. de Marignac, and C. F. Rammelsberg were rhombic bipyramids which possessed, according to the last-named savant, the axial ratios $a:b:c$ $=0·7508:1:0·3604$; and which, according to J. Traube, are isomorphous with heptahydrated sodium sulphite, $Na_2SO_3.7H_2O$. The mixed crystals of the two salts had a sp. gr. between 1·521 and 1·531, and contained $Na_2CO_3.7H_2O$; $Na_2SO_3.7H_2O=1:0·07$ to 0·45. T. Thomson gave 1·51 for the sp. gr. of the salt he prepared; he also said that it is less fusible than the decahydrated carbonate. H. Löwel's directions for preparing the stable rhombic or β-salts are:

Forty parts of the decahydrated salt are boiled in a flask with 8 to 10 parts of water until everything is dissolved, and no monohydrated salt is formed. Close the flask with a cork fitted with two glass tubes. Pour in alcohol as in the preparation of the α-salt, and keep the flask closed till the two liquids have mixed. Rectangular crystal-plates of the β-salt are formed—the growth of the crystals generally begins near the zone of contact of the two liquids. The crystals are left in contact with the alcohol six to eight days after the salt liquor has been drawn off.

The crystals of this salt prepared by T. Thomson's process were formerly stated to be *sodium octohydrated carbonate*, $Na_2CO_3.8H_2O$, but H. Löwel proved that this is a mistake; the product is sodium heptahydrated carbonate. The β-heptahydrated carbonate is less soluble than the α-salt, and more soluble than the decahydrated carbonate, so that a soln. sat. with the α-salt is supersaturated with respect to the β-salt, and the decahydrated salt. The transformation of the α- into the β-variety occurs while the salt is in contact with its mother liquid at very variable temp.—sometimes at 23°, more often below 10°. The β-salt effloresces in dry air, and passes into the monohydrated carbonate at about 32°. An appreciable amount of heat is developed during the crystallization of a supersaturated soln., and this is greater for the β-heptahydrated carbonate than for the α-salt; but less than for the decahydrated carbonate. The temp. rose from 20·5° to 22·5° during the crystallization of the β-salt from a sat. soln.

When soln. of sodium carbonate are crystallized at comparatively low temp., transparent monoclinic prisms of **decahydrated sodium carbonate,** $Na_2CO_3.10H_2O$, are formed. The range of stability is indicated in Fig. 68. According to W. Haidinger,[7] the axial ratios are $a:b:c=1·4186:1:1·4828$, and $\beta=122°\ 20'$. The crystals have been studied by H. J. Brooke, H. de Sénarmont, C. F. Rammelsberg, and A. des Cloizeaux; while J. Traube studied mixed crystals with decahydrated sodium sulphite which contain $Na_2CO_3.10H_2O:Na_2SO_3.10H_2O=1:0·13$ to 0·18, and have a sp. gr. between 1·501 to 1·502. The reported values for sp. gr.

of the crystals of decahydrated sodium carbonate range from W. Haidinger's 1·423 to F. Stolba's 1·4402 (16°); to J. P. Joule and L. Playfair's 1·454; to S. Holker's 1·455 (15·5°); to P. A. Favre and C. A. Valson's 1·456 (19°); to H. Schiff's 1·475 and to H. Schröder's 1·478; J. Dewar's value at −188° is 1·4926, and he also gives the coeff. of expansion at 17° as 0·0000787; and between −188° and 17°, 0·0001563 W. Haidinger's values for the hardness are from 1·0 to 1·5. G. J. Mulder gives the m.p. at 32·5°; H. Löwel, 34°; and H. Debray, 34·5°. According to R. Schindler, the fused salt furnishes crystals of $Na_2CO_3.H_2O$, leaving a liquid which contains more water than corresponds with $Na_2CO_3.10H_2O$, and solidifies at 33·5°. T. W. Richards and J. B. Churchill give the transition point for $Na_2CO_3.10H_2O \rightleftharpoons Na_2CO_3.H_2O+9H_2O$ at 35·2°. According to R. Schindler, decahydrated sodium carbonate effloresces rapidly in dry air, and in vacuo over sulphuric acid, it forms the monohydrated carbonate. In 1818, H. Watson noted the connection between the humidity of the air and the rate of efflorescence of decahydrated sodium carbonate. He found that when the dry-bulb thermometer registered 6° to 12°, and the wet-bulb thermometer 2·8° to 3·9° lower, a mol. of the salt lost 3·2 parts of water and none afterwards; and if the wet-bulb thermometer be 8·9° when the dry-bulb thermometer is 14·4°, the salt effloresces. On the other hand, the powdered anhydrous salt absorbed nearly 62 per cent. of water with six weeks' exposure—the salt was repulverized from time to time. R. Schindler says that the efflorescence of the salt at 12·5° furnishes pentahydrated sodium carbonate, but the product is probably a mixture of the deca- and mono-hydrated carbonates; R. Schindler says at 38°, and G. J. Mulder at 31°, the decahydrated salt forms the monohydrated salt. H. Hammerl studied the vap. press. of sodium decahydrated carbonate, and H. Lescœur, found the vap. press. at 20° to be 24·2 mm., while the vap. press. of water at the same temp. is but 17·4 mm. H. Debray says that the vap. press. of the salt is not altered when melted. The solubility of the decahydrated salt in water is indicated in Fig. 68.

According to M. Jacquelain, *sodium pentadecahydrated carbonate*, $Na_2CO_3.15H_2O$, is formed by crystallization from a supersaturated soln. at −20°, and it passes into the decahydrated salt in vacuo. M. Jacquelain's salt is possibly a mixture of ice and the cryohydrate. M. Jacquelain also reported *enneahydrated sodium carbonate*, $Na_2CO_3.9H_2O$, to be formed by passing carbon dioxide into a soln. of the normal carbonate until a little sodium hydrocarbonate separates out; and he says that the mother liquor furnishes crystals of the enneahydrated salt mixed with crystals of the hydrocarbonate. This, too, is probably a mal-interpretation.

According to A. Bérard, J. E. F. Giese, G. V. M. Fabbroni, R. Phillips, H. W. F. Wackenroder, L. A. Planche and L. R. Lecanu,[8] and A. B. Poggiale, crystals of potassium carbonate with about 20 per cent. of water crystallize from a conc. aq. soln. of potassium carbonate on long standing. The salt was accordingly regarded as *dihydrated potassium carbonate*, $K_2CO_3.2H_2O$, which has 20·6 per cent. of combined water. G. A. Städeler showed that the crystals are more readily obtained from soln. made alkaline with potassium hydroxide, and that their composition is more probably **sesquihydrated potassium carbonate,** $K_2CO_3.1\frac{1}{2}H_2O$, or $2K_2CO_3.3H_2O$. Probably to C. F. Rammelsberg, the axial ratios of the monoclinic prisms are $a:b:c=0·9931:1:0·8540$, and $\beta=111°\ 24'$. A. Kenngott and J. C. G. de Marignac have also made observations on the crystal constants. G. T. Gerlach gives the sp. gr. 2·043 at 4°. H. Lescœur found the vap. press. at 20° to be small, and at 100° about 100 mm., and from the vap. press. curve, he infers that this is the only hydrated form of potassium carbonate. The salt deliquesces in air—rapidly, according to J. J. Pohl; and only if the air is very moist, according to G. A. Städeler. J. J. Pohl also says that it dissolves in water with the evolution of heat. The solubility curve is shown in Fig. 69. L. C. de Coppet has studied the solid phases in soln. of potassium carbonate.

According to J. J. Pohl, potassium sesquihydrated carbonate loses 5·59 per cent. of water at 100°, and forms *monohydrated potassium carbonate*, $K_2CO_3.H_2O$, which at 130°–135°

loses all its water. G. J. Mulder found that the dry residue obtained by evaporating a conc. aq. soln. of potassium carbonate at 104° has about 20 per cent. of water—$K_2CO_3.2H_2O$; at 118°, 11·6 per cent.—$K_2CO_3.H_2O$; and at 133°–136°, only 0·5 to 0·8 per cent. of water remains. H. Goldschmidt patented a process for preparing what he regarded as the monohydrated carbonate by evaporating a conc. soln. at a suitable heat with constant stirring until the mass is dry. A. Morel reported that *trihydrated potassium carbonate*, $K_2CO_3.3H_2O$, is formed by cooling a warm conc. soln. of potassium carbonate below 10°. The rhombic prisms are stated to have the axial ratios $a : b : c = 0·744 : 1 : 0·384$, and to be stable in air; they are slowly dissolved by cold water and rapidly by water at 50°–60°. G. T. Gerlach prepared crystals of what he regarded as *tetrahydrated potassium carbonate*, $K_2CO_3.4H_2O$, of sp. gr. 1·997. The individuality of these three hydrated forms of potassium carbonate has not been clearly vindicated.

According to G. Kirchhoff and A. Bunsen, the evaporation of soln. of cæsium or rubidium carbonates furnishes crystals of the hydrated salt. G. Kirchhoff and R. Bunsen add that the crystals deliquesce rapidly in air, and when heated melt in their water of crystallization, and finally form the anhydrous carbonate as a white pulverulent mass, which rapidly deliquesces in air. The hydrated forms of rubidium and cæsium carbonates have not been more closely investigated.

The **solubility** of lithium carbonate in water is low: next to the phosphate and fluoride, lithium carbonate is the most sparingly soluble of the known lithium salts. L. N. Vauquelin [9] found that 100 parts of cold water dissolve one part of the salt. P. Kremers found 0·769 grm. was dissolved at 13°, and 0·778 at 102°. J. Bevad, C. N. Draper, L. Troost, A. B. Poggiale, L. Tschugaeff and W. Chlopin, A. Payen, and F. A. Flückiger give data from which it follows that the solubility per 100 grms. of soln., with Li_2CO_3 as the solid phase, is:

	0°	10°	20°	25°	30°	40°	50°	60°	80°	100°
Grms. Li_2CO_3	1·52	1·41	1·31	1·28	1·24	1·16	1·07	1·00	1·84	0·71

The solubility of sodium carbonate in water has been investigated by G. J. Mulder, H. Löwel, K. Reich, C. H. Ketner, A. Payen, etc., from which it follows that the solubility per 100 grms. of soln. is:

	0°	10°	20°	30°	32·5°	40°	60°	80°	100°	105°
Grms. Na_2CO_3	6·5	11·1	17·7	22·0	31·6	31·5	31·5	31·4	31·3	31·1
Solid phase	$Na_2CO_3.10H_2O$					$Na_2CO_3.H_2O$				

The results are plotted in Fig. 68; a more comprehensive curve, by A. Smits and J. P. Waite, is shown in Fig. 2, Cap. X. The solubilities of the two sodium heptahydrated carbonates, rhombohedral (unstable) and rhombic (stable), are:

$Na_2CO_3.7H_2O$	0°	10°	20°	30°	32·5°	35°
Rhombic	16·9	20·8	25·1	30·3	31·8	33·9
Rhombohedral	24·2	27·4	31·3	—	—	—

F. Guthrie places the cryohydric temp. at −2·10° for soln. containing 5·93 per cent. of Na_2CO_3. The curves shown in Fig. 68 are obtained by plotting the observed data. At the transition points the solubilities of the two hydrates are the same, and R. C. Wells and D. J. McAdam give 32·00° for the transition point between the deca- and stable hepta-hydrated carbonates; 35·37° for the transition point between the hepta- and mono-hydrated carbonates; and 32·96° for the metastable transition point between the deca- and mono-hydrated carbonates. The heptahydrated carbonate is solid at 35·37°, and this temp. represents an incongruent m.p. If the heptahydrated carbonate is formed, the m.p. is a congruent one, but has not been exactly determined—W. A. Tilden's approximation is 34°. C. Tomlinson and H. Löwel noticed that soln. of sodium carbonate show undercooling, and H. Löwel observed no effect when an electric current was passed through the undercooled soln. B. M. Jones has studied the crystallization of undercooled soln.

Both hydrated and anhydrous potassium carbonates deliquesce rapidly in air, forming an oily liquid formerly called *oil of tartar*, *liquor nitri fixi*, and *oleum tartari per deliquium*. R. Brandes found that anhydrous potassium carbonate absorbed

3·6 times its weight of water from sat. air in 42 days. The solubility of potassium carbonate has been determined by C. J. Mulder, L. C. de Coppet, and H. C. Dibbits. The best representative values

	0°	10°	20°	30°	40°	60°	100°	130°
Grms. K_2CO_3 . .	50·3	52·2	52·8	53·3	54·0	56·0	60·9	66·2

when the solid phase is sesquihydrated potassium carbonate, $K_2CO_3.1\frac{1}{2}H_2O$. The cryohydric temp. is $-36·5°$ for soln. containing 39·6 grms. of K_2CO_3. Both cæsium and rubidium carbonates are very soluble in water, but solubility data are not available. G. Geffcken has studied the effect of various salt additions on

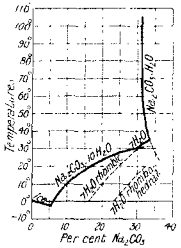

FIG. 68.—The Solubility of Sodium Carbonate in Water.

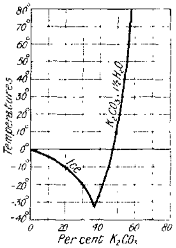

FIG. 69.—The Solubility of Potassium Carbonate in Water.

the solubility of lithium carbonate at 25°. Expressing the results in grams per litre, when the solubility in water alone at 25° is 12·63 :

Grms. of	$KClO_3$	KNO_3	KCl	NaCl	K_2SO_4	Na_2SO_4	NH_4Cl	$(NH_4)_2SO_4$
20 . .	13·10	13·3	13·5	13·9	14·7	15·0	19·2	25·0
40 . .	13·40	13·8	14·0	14·6	16·0	16·6	23·3	30·8
100 . .	—	13·5	13·9	14·2	18·2	19·4	28·4	41·0
120 . .	—	13·3	13·7	14·0	—	19·9	28·7	42·6
140 . .	—	13·0	13·3	—	—	20·4	28·8	43·5
200 . .	—	12·2	—	—	—	—	29·0	—

According to the ionic hypothesis, if the solubility product $[Li]^2[CO''_3]$ is not altered, the solubility can be increased by the union of one or other of the ions of the carbonate forming complexes with the added salt. This effect is not very marked with potassium or sodium chloride or nitrate. The marked increase in the solubility with sodium and potassium sulphates is due to the formation of lithium sulphate, but with the ammonium salts soluble complexes like $Li(NH_3)_n{}^{\cdot}$ and NH_2COO' may be formed just as is the case with magnesium carbonate in the presence of ammonium salts.

The solubility of sodium carbonate in water at first decreases, and then increases by the progressive addition of sodium chloride, and J. Kolb [10] precipitated sodium carbonate from its aq. soln. by the addition of sodium chloride. C. J. B. Karsten obtained an enamel-like product by melting the two salts together. Representing the number of grams of the respective salts—NaCl and $Na_2CO_3.10H_2O$—in 100 grms. of water, the solubility of sodium carbonate, at 15°, K. Reich found :

NaCl . . .	0	8·02	16·05	19·82	23·70	27·93	37·23
$Na_2CO_3.10H_2O$.	61·42	48·00	40·96	39·46	39·06	39·73	45·27

The last pair of numbers represents soln. with both salts in the solid phase. K. Reich represents the solubility S of decahydrated sodium carbonate in soln.

containing w grams of sodium chloride in 100 grms. of water by the expression $S=61\cdot406-2\cdot091077w+0\cdot055493w^2-0\cdot000297357w^3$ grms. of $Na_2CO_3.10H_2O$ per 100 grms. of water. This expression has a minimum with soln. containing $w=23\cdot15$ grms. of NaCl per 100 grms. of water. T. M. Chatard also studied mixed soln. of sodium chloride and carbonate. J. Kolb also made some observations on mixed soln., of *sodium sulphate* and carbonate, and *sodium hydroxide* and carbonate. R. Wegscheider and H. Walter measured the sp. gr. of mixed soln. of sodium hydroxide and carbonate, and found they followed closely the rule of mixtures for conc. not greater than 8*N*, at temp. between 10° and 80°. R. Kremann and A. Zitek studied the decrease in the solubility of sodium carbonate by additions of *sodium nitrate* and found for 100 grms. of water at 24·1°, 45·96 grms. of sodium nitrate lowered the solubility of $Na_2CO_3.10H_2O$ from 28·53 to 26·33 grms.; at 10°, 70·48 grms. of sodium nitrate lowered the solubility from 11·98 to 8·75 grms.; and at 24·2°, in the presence of 45·96, 54·43, and 62·8 grms. of sodium nitrate respectively 26·33, 24·63, and 21·8 grms. of $Na_2CO_3.7H_2O$ dissolved. If a double salt is formed, the solubility of sodium carbonate is raised, not lowered—for example, in 100 grms. of water at 10° with 35·41 grms. of *potassium carbonate*, the solubility of sodium carbonate rose from 11·98 to 17·64 grms.; and at 24·2°, with 15·00 and 22·66 grms. of potassium carbonate, the solubility of sodium carbonate rose from 28·53 to respectively 35·42 and 36·97 grms.

According to G. Gefícken, 100 grms. of aq. alcohol of sp. gr. 0·941 dissolve 0·056 grm. of lithium carbonate at 15·5°, while C. G. Gmelin says that this salt is insoluble in absolute alcohol. V. Rothmund found the solubility of lithium carbonate in water is 0·1687 mol per litre at 25°, and if the solubility in 0·125*N*-, 0·25*N*-, 0·5*N*-, and *N*-soln. of the following solvents be expressed in this order, then with the conc. expressed in mols. per litre at 25°, V. Rothmund found for *methyl alcohol*, —, 0·1604, 0·1529, 0·1395; for *ethyl alcohol*, 0·1614, 0·1555, 0·1417, 0·1203; for *propyl alcohol*, 0·1604, 0·1524, 0·1380, 0·1097; for *tertiary amyl alcohol*, 0·1564, 0·1442, 0·1224, 0·0899; for *acetone*, 0·1600, 0·1515, 0·1366, 0·1104; for *ether*, 0·1580, 0·1476, 0·1300, —; for *formaldehyde*, 0·1668, 0·1653, 0·1606, 0·1531; for *glycol*, 0·1660, 0·1629, 0·1565, 0·1472; for *glycerol*, 0·1670, 0·1647, 0·1613, 0·1532; for *mannite*, 0·1705, 0·1737, 0·1778, —; for *grape sugar*, 0·1702, 0·1728, 0·1752, 0·1778; for *cane sugar*, 0·1693, 0·1689, 0·1661, 0·1557; for *urea*, 0·1686, 0·1673, 0·1643, 0·1605; for *thiourea*, 1·1667, 0·1643, 0·1600, 0·1523; for *dimethylpyrone*, 0·1562, 0·1460, 0·1284, 0·0882; for *ammonia*, 0·1653, 0·1630, 0·1577, 0·1466; for *diethylamine*, 1·1589, 0·1481, 0·1283, 0·0937; for *pyridine*, 0·1592, 0·1503, 0·1347, 0·1091; for *piperidine*, 0·1584, 0·1488, 0·1320, 0·1009; for *urethene*, 0·1604, 0·1525, 0·1377, 0·1113, for *acetamide*, —, 0·1614, 0·1520, 0·1358; for *acetonitrile*, 0·1618, 0·1556, 0·1249, 0·1178; and for *mercuric cyanide*, 0·1697, 0·1704, —, —.

The solubilities of sodium carbonate in soln. of ethyl and propyl alcohols have been studied by C. E. Linebarger and by C. H. Ketner. The salt is just a little more soluble in *propyl alcohol* than it is in ethyl alcohol. With the ternary system—*ethyl alcohol*—water—sodium carbonate, C. H. Ketner found that two layers were formed with a critical temp. of 27·7° for a mixture with 14 per cent. of alcohol, 73 per cent. of water, and 13 per cent. of sodium carbonate, Na_2CO_3. Expressing conc. in grams of salt per 100 grms. of soln., C. H. Ketner found the results indicated in Table XLIX.

TABLE XLIX.

Solid phase.	Temp.	Alcoholic layer.			Aq. layer.		
		C_2H_5OH	Na_2CO_3	H_2O	C_2H_5OH	Na_2CO_3	H_2O
$Na_2CO_3.H_2O$	35°	62·9	0·3	36·8	1·0	32·4	66·6
	68°	55·8	0·9	43·3	2·3	28·8	68·9
$Na_2CO_3.7H_2O$	31·9°	54·8	0·7	44·5	1·7	29·8	68·5
	33·2°	58·1	0·5	42·4	1·4	31·0	67·5
$Na_2CO_3.10H_2O$	28·2°	23·5	7·3	69·2	7·9	18·6	73·5
	30·6°	47·8	1·2	51·0	2·3	27·8	69·9

H. Giraud says that potassium carbonate is insoluble in absolute alcohol. C. E. Linebarger, E. Cuno, and C. A. L. de Bruyn have measured the solubilities of potassium

carbonate in ethyl and propyl alcohols. The results with *ethyl alcohol*, water, and potassium carbonate are :

C_2H_5OH in solvent .	10	20	30	40	50	60	69	per cent.
K_2CO_3 in soln. .	*24*	*16*	*10*	*5·6*	*2·5*	*1·1*	*0·4*	,, ,,

With 40 per cent. propyl alcohol, the percentage solubility of K_2CO_3 is 4·3 ; with 50 per cent. alcohol, 2·0 ; with 60 per cent. alcohol, 0·8 ; and with 65 per cent. alcohol, 0·5. According to R. Bunsen and G. Kirchhoff, 100 grms. of absolute alcohol dissolve 0·74 grm. of rubidium carbonate at 19° ; and 11·1 grms. of cæsium carbonate at 19° or 20·1 grms. at the b.p., so that cæsium carbonate is the most soluble of the alkali carbonates in this menstruum. According to H. Arctowsky, sodium carbonate is insoluble in *carbon disulphide*. According to W. F. O. de Coninck, 100 grms. of a sat. soln. of *glycol* contain 3·28 to 3·4 grms. of sodium carbonate ; A. Vogel says 100 grms. of *glycerol* of sp. gr. 1·225 dissolve 7·4 grms. of potassium carbonate ; and A. Köhler, that 100 grms. of a sat. soln. contains 64·73 grms. of *sugar*, 6·89 grms. of sodium carbonate, and 28·38 grms. of water ; and *56·0 grms. of sugar, 22·24 grms. of potassium carbonate, and 21·76 grms. of water.*

A number of tables have been compiled showing the **specific gravity** of aq. soln., of sodium carbonate at different temp. by G. T. Gerlach,[11] J. Tünnermann, H. Schiff, R. Wegscheider and H. Walter, F. Fouqué, G. J. W. Bremer, and G. Lunge ; and for very dil. soln. by F. Kohlrausch and W. Hallwachs. The results in Table L are by G. T. Gerlach at 15° :

TABLE L.—SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM CARBONATE (15°).

	Per cent. of $Na_2CO_3.10H_2O$									
	0	1	2	3	4	5	6	7	8	9
0	—	1·0105	1·0210	1·0315	1·0420	1·0525	1·0631	1·0737	1·0848	1·0950
1	1·1057	1·1165	1·1274	1·1384	1·1495	1·058	1·062	1·066	1·070	1·074
2	1·078	1·082	1·086	1·090	1·094	1·099	1·103	1·106	1·110	1·114
3	1·119	1·123	1·126	1·130	1·135	1·139	1·143	1·147	1·150	—

G. T. Gerlach and J. Tünnermann have measured the sp. gr. of soln. of potassium carbonate. G. T. Gerlach obtained at 15° the results indicated in Table LI :

TABLE LI.—SPECIFIC GRAVITIES OF SOLUTIONS OF POTASSIUM CARBONATE (15°).

	Per cent. of K_2CO_3									
	0	1	2	3	4	5	6	7	8	9
0	—	1·00914	1·01829	1·02743	1·03658	1·04572	1·05513	1·06454	0·07396	1·08337
1	1·09278	1·10258	1·11238	1·12219	1·13199	1·14179	1·15200	1·16222	1·17243	1·18265
2	1·19286	1·20344	1·21402	1·22459	1·23517	1·24575	1·25681	1·26787	1·27893	1·28999
3	1·30105	1·31261	1·32477	1·33573	1·34729	1·35885	1·37082	1·38279	1·39476	1·40673
4	1·41870	1·43104	1·44338	1·44573	1·46807	1·48041	1·49314	1·50588	1·51861	1·53135
5	*1·54408*	*1·55728*	*1·57048*	—	—	—	—	—	—	—

The sp. gr. of a sat. soln. of lithium carbonate at 0° is 1·017 ; and at 15°, 1·014. The sp. gr. of a sat. soln. of sodium carbonate at 17·5° was given by H. Hager at 1·165 ; at 18°, by F. Kohlrausch, at 1·172 ; at 23°, by H. Schiff, at 1·222 ; and, at 30°, by G. Lunge, at 1·342. For a sat. soln. of potassium carbonate at 0°, R. Engel gives the sp. gr. 1·542.

The volume v of aq. soln. with M mols. of Na_2CO_3 in 100 c.c. of water at $\theta°$ up to 150° is given by K. Zepernick and G. Tammann as $v=1·0532+0·000773(\theta-110)+0·0000036(\theta-110)^2$ for $M=2·63$; and $v=1·0546+0·00797(\theta-110)+0·0000023$

$(\theta-110)^2$ for $M=5{\cdot}30$. G. T. Gerlach (1859) has measured the expansion of soln. of sodium and potassium carbonates; his results are shown in Table LII.

TABLE LII.—VOLUMES OF SOLUTIONS OF SODIUM AND POTASSIUM CARBONATES AT DIFFERENT TEMPERATURES.

Temp.	Sodium carbonate. Per cent. Na_2CO_3.			Potassium carbonate. Per cent. K_2CO_3.		
	5	10	15	10	30	50
0	10000	10000	10000	10000	10000	10000
5	10008	10014	10016	10011	10015	10017
10	10018·5	10029	10032·5	10025	10032	10036
15	10031	10045	10051	10038	10051	10054
20	10045	10062	10070	10053	10070	10073
30	10080	10101	10112	10088	10111	10111
40	10119	10144	10160	10128	10153	10151
50	10165	10192	10210	10173	10198	10190
60	10220	10246	10263	10226	10244	10230
70	10278	10304	10318	10282	10291	10270
80	10339	10364	10379	10342	10340	10312
100	10464	10488	10499	10465	10437	10394
B.p.	10460	10494	10510	10471	10460	10459
Temp. at b.p.	(100°·5)	101°·1	101°·18	100°·8	104°·5	115°·2

The **viscosities** of soln. of sodium and potassium carbonate have been measured by S. Arrhenius, O. Pulvermacher, W. W. J. Nicol,[12] and by A. Kanitz. The latter's values at 25° for N-, $\frac{1}{2}N$-, and $\frac{1}{8}N$-soln. are respectively 1·2847, 1·1367, and 1·0310 for sodium carbonate, and 1·1667, 1·0784, and 1·0192 for potassium carbonate. The **compressibilities** and **surface tensions** have been measured by W. C. Röntgen and J. Schneider, and the diffusion coeff. by J. Schuhmeister, and J. C. Graham. A soln. of 2·9 mols. of sodium carbonate per litre at 10°, has a **diffusion coefficient** of 0·39 sq. cm. per day; and one with three mols. of potassium carbonate per litre, 0·60 sq. cm. per day.

The **specific heat** of soln. of sodium carbonate have been determined by J. C. G. de Marignac,[13] who found that the sp. ht. of soln. with two gram-eq. of Na_2CO_3 per 50, 100, and 200 gram-eq. of water, between 21° and 26°, are respectively 0·9037, 0·9406, and 0·9675; and between 21° and 52°, respectively 0·9072, 0·9435, and 0·9695. J. Thomsen found a 2·9 per cent. soln. at 18° had a sp. ht. of 0·958. J. C. G. de Marignac also found for soln. of two gram-eq. of K_2CO_3 with 10, 50, 100, and 200 gram-eq. of water, between 21° and 52°, to be respectively 0·6248, 0·8509, 0·9157, and 1·0943.

The effect of sodium and potassium carbonates on the **vapour pressure** of water has been measured by G. Tammann.[14] Soln. of 10·16, 21·86, and 34·76 grms. of sodium carbonate, Na_2CO_3, in 100 grms. of water lower the vap. press. of water, at 29·5 mm., respectively by 1·4, 2·6, and 4·2 mm.; and soln. with 24·44, 85·9, and 136·3 grms. of potassium carbonate in 100 grms. of water lower the vap. press. of water, at 18·1 mm., respectively by 1·3, 6·3, and 9·5 mm. According to F. W. Küster and M. Grüters, the partial press. of carbon dioxide in the atm. is about 0·0004 atm., and this suffices to produce a mere trace of hydrocarbonate in any exposed soln. of sodium carbonate.

The hydrates of sodium carbonate and vapour furnish a system with two independent components, and, if one hydrate be present, the system is bivariant, and at a given temp., the hydrate can exist in equilibrium with water vapour at different press.; if two hydrates be present the system is univariant, and it is stable only when the press. at a given temp. has one unique value so that if the

press. alters one of the two hydrates becomes unstable. W. Müller-Erzbach found the vap. press. of decahydrated sodium carbonate to be 11·7 mm. at 20°, but it is not clear whether this refers to the passage from the decahydrated carbonate to the heptahydrated or to the monohydrated carbonate, but he adds that no difference was observed in the vap. press. until the salt was all converted into the monohydrated carbonate, meaning that the decahydrated carbonate passed directly to the monohydrated carbonate, or the difference in the equilibrium press. in passing from the decahydrated to the heptahydrated to the monohydrated carbonate is not great. H. Lescœur found the vap. press. of the decahydrated carbonate at 20° to be 12·1 mm in harmony with W. Müller-Erzbach's value. L. J. Andreae measured the difference in the vap. press. during the passage of the decahydrated to the heptahydrated carbonate and of the heptahydrated to the monohydrated carbonate; at 13·2°, 20·3°, and 30·5° the differences are respectively 0·79, 1·10, and 1·80 mm. W. Müller-Erzbach also gives for the range between the monohydrated and the anhydrous carbonate at 18° and 21°, 0·14 and 0·20 mm. respectively. The vap. press. of sat. soln. at the transition points, where two hydrates exist as solid phases side by side, were found by C. H. Ketner to be, at about 9°, for the deca- and hepta-hydrated salts, and for the deca- and mono-hydrated salts, to be below 5·4 mm., and for the hepta- to the mono-hydrated salt between 4·8 and 4·18 mm. Values were also obtained by H. W. Foote and S. R. Scholes, and R. E. Wilson for the vap. press. of the hydrate of potassium carbonate.

The vap. press. of the three hydrated carbonates calculated from the heats of hydration of anhydrous sodium carbonate furnishes the following relation between the absolute temp. T, and the vap. press. of the soln. in equilibrinm with the hydrates indicated by the subscript, when p denotes the vap. press. of water at $T°$ and all the press. are represented in mm. of mercury:

$$\log\frac{p_{10-7}}{p}=-\frac{393·38}{T}+1·2054\,;\qquad \log\frac{p_{10-1}}{p}=-\frac{447·64}{T}+1·3695\,;$$

$$\log\frac{p_{7-1}}{p}=-\frac{474·77}{T}+1·4423$$

These expressions give vap. press. very close to those observed by W. Müller-Erzbach, H. Lescœur, and C. H. Ketner previously indicated. The calculated differences between p_{10-7} and p_{7-1} are also close to the values observed by J. L. Andreae. Similarly for the vap. press. p_{1-0} for the reaction: $Na_2CO_3.H_2O = Na_2CO_3 + H_2O$, when the observed value at 20° is 0·18 mm.; $\log p_{1-0} = \log p - 736\,2T^{-1} + 0·528$. The results obtained by these four formulæ are plotted in Fig. 70. The space below the line AB represents the sphere of existence of anhydrous sodium carbonate; the space $BACIJ$, of the monohydrated carbonate; the space DCI, of the heptahydrated carbonate; the space DHE, the decahydrated carbonate; $FGJIHE$, of the soln. in contact with the hydrates indicated in the diagram. FG is the vap. press. curve of water. H denotes the transition points of the deca- to the hepta-hydrated salt; and I, that of the hepta- to the mono-hydrated salt. The lines represent equilibrium press. of the mixtures there indicated. H. Lescœur

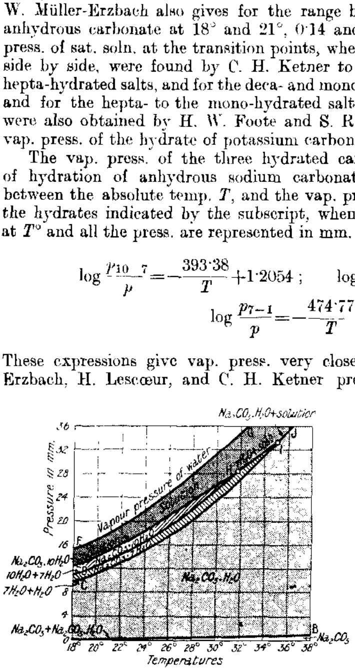

FIG. 70.—Vap. Press. of the Various Hydrates of Sodium Carbonate.

found the vap. press. of a sat. soln. of potassium carbonate to be 6·9 mm. at 20°.

G. T. Gerlach measured the **boiling points** of aq. soln. of potassium and sodium carbonates. The b.p. of soln. with 5·2, 10·4, and 51·2 grms. of Na_2CO_3 in 100 grms. of water are respectively 100·5°, 101°, and 105°; and with 22·5, 40, and 202 grms. of K_2CO_3 in 100 grms. of water, the b.p. are respectively 102°, 104°, and 133·5°. According to T. Griffiths, a sat. soln. of sodium carbonate boils at 104·5°; G. J. Mulder gives 105°; P. Kremers, 106°; and J. Legrand, 104·6°; the two latter also give the b.p. of a sat. soln. of potassium carbonate as 135°. The **freezing points** of soln. of sodium carbonate have been measured by H. C. Jones, B. M. Jones, and E. H. Loomis. The mol. depressions of the f.p. for soln. with 0·1061 and 2·122 grms. of sodium carbonate in 100 c.c. of soln. falls from 5·1° to 4·17°. The hydrolysis of the soln. stultifies the calculation of the degree of ionization of the soln. from observations on the lowering of the f.p. Similar results were obtained with soln. containing 0·1383 and 2·766 grms. of K_2CO_3 in 100 c.c. of soln. for the mol. depression fell from 5·1° to 4·39°. The lowering of the f.p. of 100 grms. of water with a gram of potassium carbonate was found by F. Rüdorff to be 0·317°; and by F. M. Raoult, 0·303°; for sodium carbonate F. M. Raoult similarly obtained 0·38°. C. M. Despretz emphasized the influence of conc. in lowering the f.p., and L. C. de Coppet examined the influence of hydrate formation on the f.p. He found that the lowering of the f.p. of aq. soln. of sodium carbonate is not proportional to the quantity of salt in soln., for with increasing conc. the lowering of the f.p. becomes less and less—thus, if Δ be the observed lowering of the f.p. with w grams of salt, the ratio Δ/w is 0·400 when w was between 1 and 3, but 0·350 when w=8. With potassium carbonate the lowering of the f.p. becomes greater and greater the more conc. the soln. Δ/w=0·300 when w=2, and 0·527 when w=60.

The **index of refraction** of dil. soln. of lithium carbonate was found by E. Doumer[15] to be μ=0·577, and the mol. index M=42·7; likewise for dil. soln. of sodium carbonate, μ=0·377, and the mol. refraction $M\mu$=40·0; and for potassium carbonate, μ=0·297, and $M\mu$=40·8. The mol. refraction for the D-line was found by J. H. Gladstone and W. Hibbert to change from 22·56 to 22·72 when the conc. of the soln. changed from 2·25 to 0·095 per cent. Na_2CO_3.

P. Burckhard and P. A. Favre and C. A. Valson found molten sodium carbonate to be a good conductor of electricity; there is an evolution of carbon dioxide at the anode, and sodium oxide with some carbon is deposited at the cathode. The **electrical conductivity** of soln. of lithium carbonate at 18° have been measured by F. Kohlrausch, and G. Vicentini.[16] Soln. containing 0·20 and 0·63 grm. of lithium carbonate in 100 grms. of soln. were found to have respectively the sp. gr. 1·0006 and 1·0050; the sp. conductivities $34·3\times10^{-4}$ and $88·5\times10^{-4}$; the eq. conductivities λ=63·5 and λ=51·9; and the temp. coeff. are 0·0249 and 0·0259 at the mean temp. 22°. The calculated value of λ_∞=106. Consequently, the estimated degree of ionization of a $\frac{1}{20}N$-soln. is 60 per cent., but the results are obscured by hydrolysis. F. Kohlrausch and E. Grüneisen found for the eq. conductivities λ, of sodium and potassium carbonates in soln. with N gram-eq. per litre:

N . . .	10	3	1	0·5	0·1	0·05	0·01	0·005	0·001
λNa_2CO_3 . .	—	27·1	45·5	54·5	72·9	80·3	96·2	102·5	112·0
λK_2CO_3 . .	18·1	55·6	70·7	77·8	94·1	100·7	115·5	120·6	133·0

The temp. coeff. of the eq. conductivity of sodium carbonate soln. for the mean temp. 22° is 0·0265; and for potassium carbonate, 0·0249. H. C. Jones and A. P. West, and C. Déguisne have also studied the temp. coeff. of the conductivity of these salts. M. H. van Laar studied the formation of sodium hydroxide by the electrolysis of soln. of sodium carbonate with and without the addition of an oxy-salt. W. Bien calculates the **transport number** for the anion in 0·05N-soln. at 23° to be 0·590, but as in the case of lithium carbonate hydrolysis interferes with the

accuracy of the result. J. Kuschel's value is 0·48. Potassium carbonate was found by G. Meslen to be diamagnetic. A. Heydweiller found for the **dielectric constant** respectively of powdered and compact anhydrous sodium carbonate, 2·97 and 8·44; 3·37 and 5·33 for decahydrated sodium carbonate; and 2·61 and 6·61 for monohydrated potassium carbonate; C. B. Thwing found 5·62 for potassium carbonate.

Aq. soln. of lithium and sodium carbonates are **hydrolyzed** and react alkaline owing to the formation of the alkali hydroxides: $Na_2CO_3+2H_2O=2NaOH+H_2CO_3$. F. C. Flückiger[17] noted in the case of the lithium salt, and H. Rose in the case of the sodium salt, that boiling soln. give off carbon dioxide. F. W. Küster and M. Grüters showed that some carbon dioxide is lost when soln. of sodium carbonate are boiled in silver vessels fitted with a silver reflux condenser; as a result, sodium hydroxide is formed. For example:

Time of boiling . .	1·25	3·5	6·0	8·5	23·25	38·0 hrs.
Na_2CO_3 undecomposed .	96·7	94·6	92·7	91·4	97·0	83·8 per cent.
NaOH formed . .	3·3	5·4	7·3	8·6	13·0	17·2 ,, ,,

This agrees with A. E. Leighton's statement that when sodium carbonate is present in water used in steam boilers, the boiled water contains sodium hydroxide. J. Shields and K. Kölichen have measured the degree of hydrolysis of aq. soln. of sodium carbonate: the former from measurements on the rate of hydrolysis of ethyl acetate, the latter from the decomposition of diacetone-alcohol, $CH_3.CO.CH_2.C(CH_3)_2OH \rightleftharpoons 2CH_3.CO.CH_3$. The percentage hydrolysis of soln. of sodium carbonate of different conc. by the two methods are of the same order of magnitude:

Gram-mol. Na_2CO_3 .	0·942	0·19	0·094	0·0477	0·0238
Per cent. hydrolysis	0·53	2·12	3·17	4·87	7·10

The first pair of numbers are by K. Kölichen, the others are by J. Shields. The results show that the degree of hydrolysis is greater, the more dil. the soln. The degree of hydrolysis also increases with temp.

The hydrolysis is represented by the equation: $Na_2CO_3+H_2O \rightleftharpoons NaHCO_3+NaOH$; followed by $NaHCO_3+H_2O=H_2CO_3+NaOH$; and by $H_2CO_3=CO_2+H_2O$. The same result is represented in the language of the ionic hypothesis: $CO''_3+H_2O \rightleftharpoons HCO'_3+OH'$; followed by $HCO'_3+H_2O=H_2CO_3+OH'$; and by $H_2CO_3 \rightleftharpoons CO_2+H_2O$ as before. All these balanced reactions are in equilibrium with one another and the soln. contains free sodium hydroxide and free carbon dioxide, and the latter, in turn, should be balanced against the carbon dioxide in the atm., or else carbon dioxide will be absorbed or evolved from the soln. according as the partial press. of the gas in soln. is greater or less than its partial press. in the atm. Soln. of sodium carbonate are known to absorb carbon dioxide from the air, showing that the partial press. of the carbon dioxide in the atm. is greater than the dissociation press. of the carbon dioxide in the soln., and this is particularly the case when soln. of sodium carbonate are boiled in open vessels exposed to flame gases rich in carbon dioxide. This is confirmed by F. W. Küster and M. Grüters, who found that the partial press. of the carbon dioxide from a normal soln. of sodium carbonate is 0·000072 atm., while the partial press. of carbon dioxide in atm. air is 0·0003 atm.; consequently, under these conditions, the soln. must absorb, not give off, gas. Consequently, the solubility will depend on the proportion of carbon dioxide in the surrounding atm.

Lithium carbonate is likewise partially hydrolyzed in soln.: $Li_2CO_3 \rightleftharpoons 2Li^{\cdot}+CO''_2$; $CO''_3+H_2O \rightleftharpoons HCO'_3+HO'$; $HCO'_3+H_2O \rightleftharpoons H_2CO_3+OH'$; and $H_2CO_3 \rightleftharpoons H_2O+CO_2$. Owing to the low solubility of lithium carbonate, its soln. are necessarily dil., with a proportionally high degree of hydrolysis—about 5 per cent. of lithium carbonate in a sat. soln. is hydrolyzed. This means that for every hundred $Li^{\cdot}$-ions there will be about ninety-five CO''_3-ions and five each of HCO'_3-ions and OH'-ions. J. Bevad found that the solubility of lithium carbonate

increased with the duration of the boiling—thus 100 grms. of water dissolved 0·80 grm. of the carbonate with 15 minutes' boiling, 0·96 grm. with 30 minutes' boiling. This is explained by assuming that carbon dioxide escapes from the soln. during the ebullition, and to restore the balance, more CO''_3-ions and HCO'_3-ions are hydrolyzed, as a result more lithium carbonate is dissolved to keep the proportion of the CO''_3-ions to that required by the solubility product. The addition of carbonic acid to the soln. decreases the proportion of CO''_3-ions, $CO''_3+H_2CO_3=2HCO'_3$ (or $Li_2CO_3+H_2CO_3=2LiHCO_3$). This means that more lithium carbonate will pass into soln. to restore the solubility product to its equilibrium value. This explains the ready solubility of lithium carbonate in carbonated water; and how lithium carbonate is reprecipitated if such a soln. is boiled because the carbon dioxide is driven from the system. Potassium carbonate, like sodium carbonate, is strongly hydrolyzed in aq. soln., and the conditions of equilibrium of the two salts appear to be analogous. Similar remarks apply to aq. soln. of rubidium and cæsium carbonates. These salts all form strongly alkaline liquids when dissolved in water.

Dry carbon dioxide has no appreciable action on dry anhydrous sodium carbonate, but if the solid or gas be moist, or if one of the hydrated forms of sodium carbonate be employed, R. Schindler [18] found that carbon dioxide is rapidly absorbed, and H. C. Kreuzberg noted that much heat is evolved, sufficient in some cases to fuse the product. Sodium hydrocarbonate, $NaHCO_3$, is the product of the reaction. According to F. Mohr and P. de Mondésir, when a little hydrocarbonate is formed, it acts as a catalytic agent on the subsequent progress of the reaction. On the other hand, sodium hydrocarbonate readily decomposes with the evolution of carbon dioxide; according to R. Kissling, dry sodium hydrocarbonate begins to decompose at about 70°, and C. S. Dyer found that the decomposition is rapid at 120°; slow at 100°; and if dry, there is scarcely any decomposition below 60°. C. S. Dyer expresses the opinion that W. B. Cowie's statement that the hydrocarbonate decomposes between 52·6° and 54·6° is based on experiments with the imperfectly dried salt. R. Schindler has shown that dry crystallized hydrocarbonate remains unchanged in dry air, but in moist air, carbon dioxide is liberated, and moisture absorbed. H. Lescœur could detect no change by keeping the dry hydrocarbonate a month over caustic baryta. A. Gautier also found that moist hydrocarbonate readily decomposes, but the dry salt did not lose 0·013 per cent. in weight when kept 30 hrs. under a press. of 15 mm. at 20°; there was a loss of 20 per cent. when kept for 4 hrs. at 100°; and the salt completely decomposed when kept 18 hrs. between 100° and 115°. A. Gautier also found that an appreciable amount of sodium hydrocarbonate is decomposed in vacuo between 25° and 30°, but no decomposition could be detected after remaining 10 hrs. between 22° and 25°. V. Urbain found the dissociation press. of sodium hydrocarbonate at 100° to be approximately 220 mm., and H. Lescœur adds that the vap. press. of decomposing sodium hydrocarbonate: $2NaHCO_3=Na_2CO_3+H_2O+CO_2$, remains constant from beginning to end, and there is no sign of the formation of an intermediate product between Na_2CO_3 and $NaHCO_3$. Similar remarks were made with respect to potassium hydrocarbonate, and H. Lescœur could find no evidence of the transition point with the sodium salt at 90·8° reported by D. W. Horn. A selection of the dissociation press. of sodium hydrocarbonate at different temp. observed by R. M. Caven and H. J. S. Sand were:

	30°	50°	70°	90°	100°	110°
Total press. . . .	9·6	40·9	150·1	481·8	826·2	1380 mm.
Press. of H_2O . . .	8·4	34·4	119·9	364·0	605·4	981·8 mm.
Press. of CO_2 . . .	1·2	6·5	30·2	117·8	220·8	399·0 mm.

R. M. Caven and H. J. S. Sand's results are higher than those obtained by H. Lescœur, and it is suggested that the latter's measurements were made on systems which are not in a state of true equilibrium. R. M. Caven and

H. J. S. Sand represent the observed vap. press. p at $T°$ K., by $\log p=11·8185-3340/T$ mm.; they also found the dissociation press. of potassium hydrogen carbonate to be 4·1 mm. at 63·7°; 56·6 mm. at 104·6°; 503·1 mm. at 147·8°; and 733·0 mm. at 156°; and they represent their observations by $\log p=10·832-3420/T$ mm. H. Lescœur found the vap. press. of this salt at 100° *remains constant during the decomposition. Similarly, the dissociation press.* p of rubidium hydrocarbonate at $T°k$ is $\log p=12·712-4300/T$ mm.; and of cæsium carbonate, $\log p=16·930-6300/T$ mm. The observations with the four hydrocarbonates are summarized in Fig. 71. The constancy of the vap. press. of sodium hydrocarbonate noted by H. Lescœur does not necessarily prove that no trona, $Na_2CO_3.NaHCO_3.2H_2O$, is formed, $5NaHCO_3=Na_2CO_3.NaHCO_3.2H_2O+Na_2CO_3+2CO_2$, because, according to the phase rule, a system with four phases and three components is tervariant, so that all combinations between $NaHCO_3$ and trona, $Na_2CO_3.NaHCO_3.2H_2O$, must exercise the same press. Trona is stable at *ordinary temp., and at 100° it gives an approximately constant press. of 496 mm.* until the greater part of the water, and but little carbon dioxide, is lost; the press. then drops to 182 mm., where it remains until all is converted into anhydrous sodium carbonate. The dissociation press. of the alkali hydrocarbonates show that their stabilities towards heat increase with rise of at. wt. of the metal, but the change in passing from potassium to the sodium salt is markedly different from that between any other two elements. Some partially decomposed hydrocarbonate gave a press. of 800 mm.; this then fell to approximately 189 *mm., and later on to the same value as trona.* M. Soury heated a mixture of 27·54 grms. of sodium hydrocarbonate to 100°, and measured the press. after the removal of carbon dioxide in successive portions. The total volume of carbon dioxide obtainable from the above mixture is 3660 c.c. The tension of the carbonic acid decreases as fast as the carbon dioxide is progressively removed, but there are two periods of constant press.: (1) from the removal of 260 to 1760 c.c. of the dioxide; (2) from 2560 to 3210 c.c. In the first case, the two solid phases are the hydrocarbonate and a lower carbonate of the composition $3Na_2O.4CO_2.5H_2O$; at the second period of constant press. the solid phases are in all probability the salt last mentioned and the normal carbonate, $Na_2O.CO_2.H_2O$.

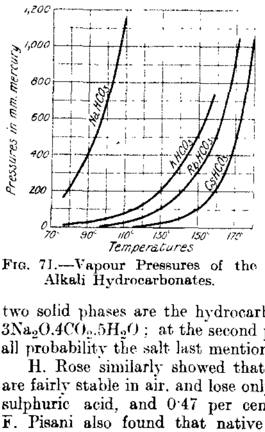

FIG. 71.—Vapour Pressures of the Alkali Hydrocarbonates.

H. Rose similarly showed that the dry crystals of potassium hydrocarbonate are fairly stable in air, and lose only 0·05 per cent. when kept 24 hrs. in vacuo over sulphuric acid, and 0·47 per cent. in air confined over potassium hydroxide. F. Pisani also found that native potassium hydrocarbonate, kalcinite, are not changed by exposure to air. D. Gernez found very little potassium hydrocarbonate is decomposed in a closed vessel at 10°, but in a stream of inert gas—air, hydrogen, or nitrogen—carbon dioxide is slowly removed, and normal potassium carbonate is formed. When heated to 190° or 200°, M. Jacquelain says the crystals are completely decomposed: $2KHCO_3=K_2CO_3+CO_2+H_2O$. A. Gautier says that dry potassium hydrocarbonate does not decompose in vacuo at 22°–25°, but does appreciably decompose at 25°–30°. H. C. Dibbits says that the potassium salt decomposes more rapidly than the sodium salt because the normal carbonate is deliquescent and forms a soln. with the undecomposed hydrocarbonate which readily decomposes. A. Gautier says that potassium hydrocarbonate decomposes more slowly than the sodium salt at 100°, and M. Ballo made a similar observation at 98°, and he noted that at 98° the loss per hour was 0·29 per cent., and at 135°, 8·43 per cent. It is sometimes argued that the formation of normal sodium carbonate

by the calcination of *solid* sodium hydrogen carbonate proceeds at too low a temp. to make it probable that the sodium atom of one mol. displaces the hydrogen atom of another mol. It is considered that the reaction must be *intra-* not *inter-*mol. Hence, the mol. is represented $(NaHCO_3)_2$, or as a double salt of sodium carbonate and carbonic acid, $Na_2CO_3.H_2CO_3$.

Although dry sodium hydrocarbonate requires but a moderate heat for its decomposition, it is fairly stable at ordinary temp.; aq. soln. are less stable than the dry salt. J. W. Döbereiner noticed that when a soln. of sodium hydrocarbonate is evaporated rapidly in vacuo about one-fourth of the carbon dioxide is lost. R. Schindler said that a soln. of the salt in 14 times its weight of water, is not changed in air; but if a small proportion of water be present, the hydrocarbonate loses carbon dioxide in air, even below 0°, and this the more rapidly the higher the temp., until nothing but the normal carbonate remains. H. Rose found that a soln. of sodium hydrocarbonate loses carbon dioxide when evaporated at ordinary temp. over conc. sulphuric acid and potassium hydroxide. If the residue be dissolved in water and again evaporated a residue of the normal carbonate almost free from the hydrocarbonate is obtained. H. Rose also noted that by boiling the aq. soln. half the contained carbon dioxide can be driven off so that the normal carbonate remains. H. Rose further found that aq. soln. of potassium hydrocarbonate behave similarly, but decompose even more rapidly than soln. of sodium hydrocarbonate. R. Bunsen and G. Kirchhoff also noted that soln. of rubidium and cæsium hydrocarbonates readily lose carbon dioxide when boiled. C. G. Gmelin and C. F. Rammelsberg observed likewise that soln. of lithium hydrocarbonate give the normal carbonate when allowed to stand in air or when evaporated to dryness. G. Magnus removed carbon dioxide from a soln. of sodium hydrocarbonate, at ordinary temp., by a stream of hydrogen; and R. F. Marchand obtained a similar result at 0° by a stream of 1.5×10^6 c.c. air. At 38° R. F. Marchand converted 95 per cent. of the hydrocarbonate into the normal carbonate by aspirating 2×10^6 c.c. of air through the soln., and concluded that all would have been transformed had the action been sufficiently prolonged. H. C. Dibbits made some experiments on the equilibrium press. of sodium and potassium hydrocarbonates in sat. aq. soln. He found

	15°	30°	40°	50°
Press., $NaHCO_3$ . .	120	212	356	563 mm.

Soln. of the alkali hydrocarbonates have a feebly alkaline reaction. F. W. Küster, and F. P. Treadwell and M. Reuter showed that the soln. of sodium hydrocarbonate at ordinary temp. colours phenolphthalein red, but, in consequence of the reversal of the hydrolysis, the coloration disappears when the temp. approaches 0°. Potassium hydrocarbonate is almost neutral towards phenolphthalein but at great dilutions, the soln. have an alkaline reaction: $KHCO_3+H_2O \rightleftharpoons KOH+H_2O+CO_2$. The partial press. of the carbon dioxide is therefore greater in dil. than in conc. soln., and in hot than in cold soln. F. P. Treadwell and M. Reuter also made some determination of the composition of a $\frac{1}{10}N$-soln. of sodium hydrocarbonate when the partial press. varied from 2 to 4 per cent. of an atm. H. C. Dibbits pointed out the errors which have arisen in measuring the solubility of sodium hydrocarbonate owing to the lack of precautions to prevent the loss of carbon dioxide and consequent formation of the normal carbonate, so that the results represented not the solubility of the hydrocarbonate, but rather a mixture of this salt with an indefinite proportion of the normal carbonate. G. Lunge, I. Rosenthal and F. K. Cameron have emphasized the loss of carbon dioxide by soln. of sodium hydrocarbonate in connection with analysis of carbonates, hydrocarbonates, and gases containing carbon dioxide.

A soln. of sodium carbonate, Na_2CO_3, absorbs carbon dioxide from the atm., forming some hydrocarbonate, $NaHCO_3$, and F. K. Cameron and L. J. Briggs studied the formation of sodium hydrocarbonate in soln. of the normal carbonate and found equilibrium was attained in about a week's time. The higher the temp.

and the more conc. the soln., the less the percentage conversion; at 100°, very little hydrocarbonate is formed. H. M. McCoy also investigated the conversion of carbonate to hydrocarbonate by air containing different proportions of carbon dioxide. in soln. at 25° barometer 712 mm. Fig. 72 shows H. M. McCoy's equilibrium curves for sodium carbonate and hydrocarbonate in soln. of different conc., and in atm. containing different amounts of carbon dioxide. The partial press. of the carbon dioxide in atm. is indicated in the respective curves. From these results it follows that at 25° in air in which the carbon dioxide has normally a partial press. of 0·00028 atm. a considerable proportion of hydrocarbonate is present when a soln. of sodium carbonate has assumed a state of equilibrium. It also follows that a soln. of the hydrocarbonate is unstable in atm. air, for a normal hydrocarbonate soln. loses carbon dioxide until but 12 per cent. of the sodium is present in equilibrium as hydrocarbonate. With higher partial press. of carbon dioxide a larger proportion of hydrocarbonate remains undecomposed. Raising the temp. lessens the proportion of hydrocarbonate which can exist in soln. in equilibrium with air. G. Bodländer and P. Breull have shown that the soln. is stable if an excess of carbon dioxide be present. Only 0·04 per cent. of the salt is decomposed if the soln. be sat. with carbon dioxide—the solubility of sodium hydrocarbonate is much influenced by the amount decomposed, and satisfactory data can be obtained only when the press. of the carbon dioxide is constant. V. Urbain found that the dissociation of sodium hydrocarbonate is retarded when the soln. contains sugar or gum. The addition of sodium hydrophosphate helps to control the neutrality of soln. for medicinal purposes.

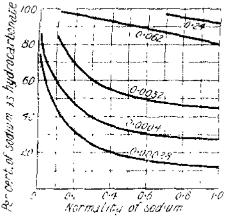

FIG. 72.—Equilibrium Curves: $NaHCO_3 + H_2O \rightleftharpoons NaOH + H_2CO_3$.

Representing conc. by the symbols of the compounds in brackets, L. T. Henderson and O. F. Black have shown that in mixed soln. of the two salts, $k_1[NaH_2PO_4]/[Na_2HPO_4] = k_2[H_2CO_3]/[NaHCO_3]$, where $k_1 = 2·5+10^{-7}$ and $k_2 = 3·8+10^{-7}$. The loss of carbon dioxide by soln. of the hydrocarbonate is conditioned by (i) the weakness of carbonic acid, H_2CO_3, as an acid; (ii) the acid character of sodium hydrocarbonate; (iii) the ready dissociation of carbonic acid; and (iv) the low solubility of carbon dioxide in water so that the carbonic acid existing in soln. necessitates a certain gaseous press. of carbon dioxide; and the ratio of the two represents the solubility of the gas. In a system containing a dil. soln. of sodium hydrocarbonate and vapour, the conc. of the carbon dioxide in the vapour is a measure of the carbon dioxide in the soln., but the conc. of the carbon dioxide in the vapour is not a measure of the degree of hydrolysis: $NaHCO_3 + H_2O \rightleftharpoons NaOH + H_2CO_3$, because equilibrium is much more complex than this. For instance, sodium hydrocarbonate acts as an acid on the sodium hydroxide: $NaHCO_3 + NaOH \rightleftharpoons Na_2CO_3 + H_2O$. If C_1 represents the conc. of the sodium hydrocarbonate; C_2, of normal sodium carbonate; C_3, of sodium hydroxide; and C_4, of carbonic acid, the condition of equilibrium in the reaction $NaHCO_3 + H_2O \rightleftharpoons NaOH + H_2CO_3$, as $C_3C_4 = K_1C_1$, where K_1 is the dissociation constant or the constant of proportion; similarly for $NaHCO_3 + NaOH \rightleftharpoons H_2O + Na_2CO_3$, $C_1C_3 = K_2C_2$. By combining these two results, it follows that $C_1^2/C_2C_4 = K_2/K_1 = K$, the equilibrium constant of the system. G. Bodländer obtained an analogous expression for dil. soln. on the ionic hypothesis. The conc. of the carbon dioxide in soln. if equal to the product of the partial press. p of the carbon dioxide in the atm. and the solubility constant k, so that $C_4 = kp$. Again, if one mol. of sodium hydrocarbonate be dissolved in v litres of water, and when equilibrium is attained x mols. of hydrocarbonate remain unchanged, so that $C_1 = x/v$; and $1-x$ mols. of

hydrocarbonate are converted into $\frac{1}{2}(1-x)$ mols. of normal carbonate, so that $C_1=\frac{1}{2}(1-x)/v$. If, therefore, C denotes the conc. of the sodium in gram-atoms per litre, $C=1/v$, and $C_1^2=KC_2C_4$, or $2x^2C=kp(1-x)K$. A litre of water at 25° dissolves 0·8256 litre or 0·0338 mols. of carbon dioxide at 25° and 760 mm., so that k=0·0338. For dil. soln., H. N. McCoy found that k is very nearly 5300—for example, with a soln. 0·0999N with respect to the sodium, when x=0·682, and p, 0·00161, k, 5320.

J. Walker and W. Cormack found the ionization constant of carbonic acid $[H][HCO_3']=k_2[H_2CO_3]$ to be $k_2=3·04\times10^{-7}$. J. Kendall's value for k_2 at 0° is $2·24\times10^{-7}$; at 18°, $3·12\times10^{-7}$; and at 25°, $3·5\times10^{-7}$. The value of the second ionization constant, $[H^{\cdot}][CO_3'']=k_3[HCO_3']$, is not so clear. H. N. McCoy determined the ratio $k_2/k_3=[HCO_3']^2/[CO_3''][H_2CO_3]$, and J. Shields determined the ratio $k_w/k_3=[HCO_3'][OH]/[CO_3'']$ from experiments on the hydrolysis of ethyl acetate; F. Auerbach and H. Pick used a colorimetric process for the ratio k_w/k_3, where k_w is the ionization constant for water. At 25°, H. N. McCoy gives $k_w=1·2\times10^{-14}$; F. Auerbach and H. Pick, $1·05\times10^{-14}$; C. W. Kanolt, $0·82\times10^{-14}$; F. C. Frary and A. H. Nietz, $1·76\times10^{-14}$; and J. Johnston, and G. N. Lewis and M. Randell, $0·8\times10^{-14}$. C. A. Seyler and P. V. Lloyd found $k_3=4·27\times10^{-11}$ at 25°, so that the ratio $k_2/k_3=7124$, and $k_w/k_3=19·2\times10^{-5}$. The numerical values of two ratios k_2/k_3 and k_w/k_3 increase on dilution, but not in the same proportion. C. A. Seyler and P. V. Lloyd showed that the apparent variations in the second ionization constant are due to the ionization of sodium hydrocarbonate (α) and of *normal* sodium carbonate (β). If k_c be the value of the ratio $[NaHCO_3]/[Na_2CO_3][H_2CO_3]$, and k_d that of the ratio $[NaHCO_3][OH]/[Na_2CO_3]$, and if the ionization of the hydrocarbonate and carbonate be respectively α and β, $k_2/k_3=k_c\alpha^2/\beta$; and $k_w/k_3=k_d\alpha/\beta$, so that k_c and k_d do not increase proportionally. J. Stieglitz assumed the ionization constant α of the hydrocarbonate to be the same as that of sodium acetate, at the same mol. conc., and this was confirmed by C. A. Seyler and P. L. Lloyd either alone or in the presence of chloride or carbonate. J. Stieglitz assumed that the ionization constant β of sodium carbonate is nearly the same as that of the sulphate, so that β=0·687 for a conc. 100×10^{-3}; and β=0·584 for a conc. 300×10^{-3}. W. D. Harkins estimates β=0·598 for a conc. 100×10^{-3}, and β=0·420 for a conc. 1000×10^{-3}. F. Auerbach and H. Pick assume β=0·60 for a conc. 95×10^{-3}. C. A. Seyler and P. V. Lloyd estimate that the value of β, the ionization of sodium carbonate (in respect of the CO_3-ion) between eq. conc. 1000×10^{-3} and 100×10^{-3} (and probably at higher dilutions) may be approximately represented by the empirical formula $\beta=1·104-0·320\log C$, where C is the sodium conc. in milligram-eq. per litre. In the presence of sodium chloride, the apparent value of β is greater than for pure bicarbonate and carbonate soln. at the same sodium conc. If r is the ratio of sodium as chloride to sodium as bicarbonate and carbonate, then $\beta=(1·104-0·320\log C)\{1-0·1512\log(r+1)\}/\{1-0·3096\log(r+1)\}$. These values are less than those estimated for the conductivity of sodium sulphate. C. A. Seyler and P. V. Lloyd found that sodium carbonate ionizes in two stages. In the first stage, $Na_2CO_3\rightleftharpoons Na^{\cdot}+NaCO_3'$, where the ionization constant is $k_a=[Na][NaCO_3]/[Na_2CO_3]$. In the second stage, $NaCO_3'\rightleftharpoons Na^{\cdot}+CO_3''$, in which the ionization constant $k_b=[Na][CO_3]/[NaCO_3]$ is smaller and more constant than the first. The numerical values of these constants for soln. with the conc. C=50. 200, and 500 milli-eq. of Na per litre, are k_a=0·1060, 0·2590, and 0·3760 respectively when k_b=0·0870, 0·1240, and 0·1190.

H. Moissan[19] found that sodium carbonate is attacked by **fluorine** in the cold. H. Quantin showed that when sodium carbonate and **carbon tetrachloride** are heated together, sodium chloride, carbon dioxide, and carbonyl chloride are produced. M. J. Fordos and A. Gélis obtained a mixture of sodium sulphide and thiosulphate by heating an intimate mixture of the sodium carbonate and **sulphur** to 275°; while H. E. Schöne says that if the mixture is fused, a mixture of sodium trisulphide and sulphate is formed. J. B. Senderens found that sulphur acts slowly on a soln.

of potassium carbonate at ordinary temp., but rapidly if boiled, forming the thiosulphate and a polysulphide ; if the reaction is allowed to proceed in a sealed tube there is but little change because of the counter-reaction. According to J. Sauerschnig, **hydrogen sulphide** partially displaces the carbon dioxide from soln. of potassium carbonate, forming a mixture of potassium hydrocarbonate and hydrosulphide. M. Berthelot obtained a mixture of potassium sulphide and sulphate by passing **sulphur dioxide** over potassium carbonate heated to redness. A. Terreil says **antimony sulphide** has no action on a soln. of potassium carbonate, but with sodium carbonate, the mineral kermes is produced. In the dry way, potassium produces more mineral kermes than the sodium salt. The alkali carbonates are all decomposed by **acids** with the liberation of carbon dioxide ; and when fused with **silica, titanic oxide,** or **zirconia,** carbon dioxide is likewise liberated. With **boric acid** a metaborate is formed ; with **alumina,** an aluminate ; and, according to F. G. Schaffgotsch, **ferric oxide** ; and, according to A. Stromeyer, **ferrous oxide,** drive out the carbon dioxide from fused sodium carbonate, and form a green mass of alkali ferrite. E. Kopp found that **ferrous sulphide** under similar condition, gives a mixture of carbon monoxide and dioxide gases in the proportions 1 : 3, and forms a very dark-green mass which dissolves in water forming a dark-brown soln. which turns dark green on exposure to air and contains sodium hydroxide and a double sulphide of sodium and iron. Sodium and potassium carbonates are reduced by **carbon** at a high temp., and, early in the nineteenth century, the metals were prepared by this reaction. Lithium carbonate under similar conditions forms lithia, not the metal, but if heated in an electric furnace with an excess of carbon, it forms a carbide, $Li_2CO_3+4C=Li_2C_2+3CO$, and in this respect it resembles the alkaline earth rather than the alkali family. E. Vigouroux found the alkali carbonates form silicates when fused with **silicon.** As previously indicated, the salt is decomposed when heated in a stream of **hydrogen,** but, according to K. Stammer, not by **carbon monoxide.** L. Frank found that sodium is also produced when the carbonate mixed with **aluminium powder** is heated in a stream of hydrogen. According to G. Dragendorff, when a mol. of sodium carbonate is heated to redness with six gram-atoms of **phosphorus,** sodium phosphate, carbon, and carbon monoxide are formed : $2P+3Na_2CO_3=2Na_3PO_4+2C+CO$—the reaction begins at 220°, and if completed at 240°, a brown substance resembling humus is produced instead of carbon—possibly an unstable carbon phosphide is formed at the lower temp. E. C. Franklin and C. A. Kraus report that sodium carbonate is insoluble in liquid **ammonia.** H. Giraud found that a conc. soln. of potassium carbonate sat. with ammonia separates into two layers—the upper one contains almost all the ammonia, and the lower one the potassium carbonate. The latter is virtually insoluble in the ammonia soln. The two layers coalesce when heated in a sealed tube, but separate again on cooling. R. Abegg and H. Riesenfeld found the vap. press. of a normal soln. of ammonia at 25° to be 13·45′ mm., and in the presence of $\frac{1}{2}N$-, N-, and $1\frac{1}{2}N$-K_2CO_3, the vap. press. rose respectively to 17·10, 20·75, and 24·40 mm. For the action of the hydroxides of the alkaline earths, see the alkali hydroxides.

According to F. A. Flückiger, lithium forms a basic carbonate ; *lithium oxycarbonate* is a crystalline compound of lithium oxide and carbonate whose composition and limits of existence have not been explored. According to H. le Chatelier, the fusion curve of mixtures of potassium and lithium carbonates shows two eutectics, one at 500° and the other at 492°, corresponding respectively with 26 and 46·6 per cent. of lithium carbonate. The intermediate maximum at 515° corresponds with the formation of the double salt, **lithium potassium carbonate,** $LiKCO_3$.

E. Mitscherlich [20] found that an intimate mixture of potassium and sodium carbonates fuses at a lower temp. than either salt alone, and F. Stolba found that at ordinary temp. the sp. gr. of the fused mass was 2·53–2·56. H. le Chatelier obtained the V-eutectic at 690° with 48·5 per cent. Na_2CO_3 with no sign of the formation of a compound of the two salts at fusion temp. These facts of course do not prove the formation of a chemical

individual as a complex of the two salts; indeed, as previously indicated, P. Niggli found that a series of mixed crystals is formed under these conditions. F. Margueritte claimed to have obtained a double carbonate by the repeated crystallization of the mother liquor obtained in the manufacture of potassium ferrocyanide, and by conc. a soln. containing a mixture of the two carbonates with an excess of the potassium salt. J. C. G. de Marignac obtained large crystals of what he regarded as a double salt in a similar manner; and added that if the soln. be conc. in vacuo, crystals of monohydrated sodium carbonate, $Na_2CO_3.H_2O$, are alone obtained. The salt has also been obtained by F. Stolba, and by W. Graff from the potash obtained as a by-product in the manufacture of beet sugar.

The composition of F. Margueritte's crystals formed from soln. with an excess of potassium carbonate corresponds with octodecahydrated sodium potassium tricarbonate, $K_2CO_3.2Na_2CO_3.H_2O$. According to J. C. G. de Marignac, and F. Stolba, the monoclinic crystals formed from approximately equi-molecular proportions of the two carbonates, have the composition of *hexahydrated sodium potassium carbonate*, $KNaCO_3.6H_2O$. The axial ratios measured by the former were $a : b : c = 0.9645 : 1 : 0.8143$, and $\beta = 131° 48'$. The crystals have also been measured by A. Knop, and by V. von Zepharovich; the latter showed that the habit of the crystals is very sensitive to the composition of the soln. The solubility of mixtures of the two salts at 25° shows no signs of the formation of any other double salt than $Na_2CO_3.K_2CO_3.12H_2O$. F. Stolba says the crystals are decomposed by recrystallization from water, and that crystals richer in sodium crystallize from the soln. unless an excess of the potassium salt be added to the soln. F. Stolba also says that 100 grms. of water at 12·5° dissolve 133·3 grms. of the salt, and at 15°, 185·2 grms. of the salt—the latter soln. has a sp. gr. 1·366. F. Stolba found the sp. gr. of the crystals to be 1·61–1·63 at 14°. H. von Fehling says the crystals are slightly hygroscopic, and effloresce in dry air; they lose almost all their water at 100°. L. Hugounenq and J. Morel say the spontaneous crystallization of soln. containing 495·9 grms. of potassium iodide; 10·3 of potassium carbonate; 77·3 of sodium carbonate; 42·0 of disodium hydrophosphate; and 58·3 of sodium chloride furnish monoclinic prisms with axial ratios $a : b : c = 0.7104 : 1 : 0.7800$, and $\beta = 104° 25'$. The crystals have the composition *dodecahydrated potassium trisodium dicarbonate*, $KNa_3(CO_3)_2.12H_2O$, or $KNaCO_3.Na_2CO_3.12H_2O$, or $K_2CO_3.3Na_2CO_3.24H_2O$. The crystals effloresce in air, they melt in their water of crystallization at 40°, and dissolve in their own weight of water. When recrystallized from water, the composition of the product approximates closely to F. Margueritte's salt. The composition of the crystals is so sensitive to the composition of the soln. that L. Hugounenq and J. Morel concluded that mixed crystals and not true double salts are produced.

E. Brunner found the following conditions obtain between fused sodium and alkali carbonates and chlorides or bromides at 900°: 52 per cent. of $(KCl+\frac{1}{2}Na_2CO_3) \rightleftharpoons 48$ per cent. of $(NaCl+\frac{1}{2}K_2CO_3)$; 63 per cent. of $(KCl+\frac{1}{2}Li_2CO_3) \rightleftharpoons 37$ per cent. of $(LiCl+\frac{1}{2}K_2CO_3)$; 53 per cent. of $(KBr+\frac{1}{2}Na_2CO_3) \rightleftharpoons 47$ per cent. of $(NaBr+\frac{1}{2}K_2CO_3)$; 56 per cent. of $(NaCl+\frac{1}{2}Li_2CO_3) \rightleftharpoons 44$ per cent. of $(LiCl+\frac{1}{2}Na_2CO_3)$.

M. Amadori studied fused mixtures of sodium fluoride and carbonate: no compound is formed, and the salts are not miscible in the solid state. There is a eutectic at 690° and 39 mols. per cent. sodium fluoride. Similar results obtain with sodium chloride and carbonate. There is an eutectic at 636° and 59 mols. per cent. of sodium chloride. Similarly, with potassium fluoride and carbonate, there is with a eutectic at 636° and 65 mols. per cent. of potassium chloride. With the system potassium fluoride and carbonate there is a eutectic at 688° with nearly 46 mols. per cent. of potassium fluoride, and another eutectic at 682° with 62 mols. per cent. of potassium fluoride; there is a slight rise in the m.p. between the two eutectics, corresponding with the formation of **potassium fluorocarbonate,** $KF.K_2CO_3$.

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§ 32. The Alkali Hydrocarbonates, Bicarbonates, or Acid Carbonates

A. Arfvedson noticed that the solubility of lithium carbonate in water is increased if the water be sat. with carbon dioxide; the solubility is increased nearly five-fold, for L. Troost[1] found that under these conditions, the solubility in 100 grms. of water is 5·25 grms.; A. Goldammer gives 5·45 grms.; and J. Bevad, 5·501 grms. at 13°. P. Carles also found the solubility of lithium carbonate is augmented if alkali hydrocarbonates are present in the soln. A. Arfvedson found that a crystalline crust is obtained by the evaporation of the soln. of lithium carbonate in carbonated water, the product was shown by C. G. Gmelin, and C. F. Rammelsberg to be normal lithium carbonate. **Lithium hydrocarbonate** has not therefore been isolated, although there is little doubt about its existence in aq. soln.—*q.v.* P. N. Raikow says that a soln. of lithium carbonate does not absorb enough carbon dioxide to convert all the normal salt into the hydrocarbonate.

The direct product of the ammonia-soda process and its modifications is **sodium hydrocarbonate**, $NaHCO_3$; and as indicated in connection with the occurrence of sodium carbonate, it occurs in alkaline spring waters; in association

with the normal carbonate as trona and urao; but not alone as sodium hydrocarbonate. When carbon dioxide is passed through a soln. of sodium carbonate in twice its weight of water, sodium hydrocarbonate is precipitated, but the absorption of the gas is slow at ordinary press., and therefore H. C. Kreuzburg recommended working with the gas under press. L. Meyer has studied quantitatively the absorption of carbon dioxide by soln. of sodium carbonate, and the relations between carbon dioxide and sodium carbonate and hydrocarbonate have been previously discussed. L. Pesci claims to have prepared potassium or sodium hydrocarbonate free from the chloride or nitrate by the following process:

A soln. of potassium hydroxide or sodium carbonate in 80 per cent. alcohol is sat. with carbon dioxide. At first, normal carbonate is formed which withdraws the water from the alcohol, forming a dense stratum at the bottom of the vessel, but on continuing the passage of the gas this becomes pasty from deposition of crystals of the hydrocarbonate. The alcohol, containing chlorides and nitrates, is now decanted and replaced by a fresh quantity, the passage of the gas being continued, with occasional agitation, until the pasty precipitate becomes pulverulent and the liquid is sat. with carbonic anhydride. The hydrocarbonate, after being thoroughly washed with alcohol, is found to be quite pure.

It is formed under many conditions when powdered and moist solid sodium carbonate or one of the hydrates is exposed to the action of carbon dioxide. H. C. Kreuzburg, W. Mählenbrook, J. J. Berzelius,[2] F. Mohr, F. Schäffer, P. de Mondésir, W. F. W. Artus, W. F. Channing, and M. Jacquelain used this method of preparation. R. Smith and P. F. G. Boullay pointed out that the spongy friable mass so obtained must be pulverized and repeatedly washed with cold water to free it from the unconverted carbonate; and R. Schindler, that the salt must be rapidly dried after washing because it loses carbon dioxide rapidly if exposed in a moist condition to the air, or it may be dried at 37°, and once more exposed to the action of the gas. R. Schindler also adds that if the salt be fully sat. with carbon dioxide it no longer reddens turmeric nor gives a precipitate with a very dil. soln. of mercuric chloride, but with a conc. soln., a white precipitate is formed which in a few minutes becomes red and then purple; if the least amount of normal carbonate be present, the precipitate is reddish-brown. T. Bergmann described this reaction in 1774. If some ammonium carbonate be present, the precipitate with normal carbonate is white. G. Patein noted that sodium hydrocarbonate gives no precipitate with a soln. of magnesium sulphate. E. Biltz says that the first effect on mixing eq. quantities of sodium hydrocarbonate and mercuric chloride is the formation of a white opalescence, then a reddening of the liquid, and the formation of a dark-red precipitate of $2HgCl_2.3H_2O$. H. Hager says that mercurous chloride succeeds better than mercuric chloride; if 0·5 grm. of mercurous chloride, 1·0 grm. of sodium hydrocarbonate, and 1·5 grms. of water be shaken together, no darkening occurs in the absence of normal sodium carbonate, but if the last-named salt be present a more or less intense grey coloration appears. Sodium hydrocarbonate can be prepared by the action of ammonium carbonate on sodium carbonate. F. Schäffer allowed an intimate mixture of commercial ammonium carbonate with three to four times its weight of decahydrated sodium carbonate to stand for 24 hrs. with the slurry-like mass exposed to the sun on absorbent paper or porous tiles. The last traces of ammonia escape with the water, and a chalk-like mass of sodium hydrocarbonate remains. According to R. Schindler, a mixture of sodium monohydrated carbonate with two-thirds its weight of ammonium carbonate, when exposed to air between 25° and 30°, gives off unchanged ammonium carbonate and furnishes normal sodium carbonate, but at 75°, the mixture gives off ammonia and leaves a residue of sodium hydrocarbonate. F. L. Winckler recommended modifications of the ammonium carbonate process. J. N. Planciva prepared sodium hydrocarbonate by the action of sulphuric acid on a soln. of sodium carbonate; R. Schindler used acetic acid.

A bottle containing a soln. of 286·4 grms. of decahydrated sodium carbonate dissolved in twice its weight of water is closed by a stopper fitted with a tube-funnel drawn to a very

fine tip, and dipping about an inch below the surface of the soln. 49 grms. of sulphuric acid are carefully poured through the funnel. The mixture is allowed to stand without *agitation for several days. Crystals of sodium hydrocarbonate are formed.* These are collected, washed, and dried. The finer the tip of the tube-funnel, adds R. Schindler, and the more slowly the sulphuric acid runs into the liquid, the better the crystals; the least shaking is disadvantageous since carbon dioxide is thereby evolved. If acetic acid be used, some shaking is needed.

The corresponding **potassium hydrocarbonate,** $KHCO_3$, was reported by F. Pisani[3] to occur at Chypis (Canton Wallis) as a mineral which he called *kalicine* or *kalecinite*, with the composition: K_2O, 42·60 per cent.; MgO, 0·64; CaO, 1·40; CO_2, 44·00; H_2O, 7·76; sand, etc., 3·60. It is obtained by similar processes to those employed for the sodium salt. F. A. Cartheuser, M. Weitzel, and F. Mohr made it by passing carbon dioxide into a conc. soln. of potassium carbonate when the sparingly soluble hydrocarbonate crystallizes out. The absorption of the gas is slow at first, but proceeds more quickly the more conc. the soln., and F. Wöhler used solid potassium carbonate moistened with a little water. The carbonate was made in a porous form by the ignition of the tartrate, and the vessel was kept cool by surrounding it with cold water because during the absorption of the carbon dioxide much heat is evolved. The crystals of the hydrocarbonate were treated with a little water at 60°, filtered, and, on cooling, most of the hydrocarbonate separates in large crystals. A. Duflos used an analogous process. H. C. Kreuzburg treated potassium carbonate moistened with alcohol in a similar manner. F. A. Cartheuser also made potassium hydrocarbonate by the action of ammonium carbonate on a conc. soln. of the normal carbonate. A. Duflos, W. H. S. Buchholz, and J. B. Trommsdorf used a similar process. M. Sehlmeyer and I. Fölix mixed a conc. soln. of potassium carbonate at 75° with barely enough acetic acid or cream of tartar to sat. all the potassium. The acid is added gradually, and so soon as the soln. begins to efferversce, it is filtered, and crystals of the hydrocarbonate separate out on cooling.

R. Bunsen and G. Kirchhoff[4] made **rubidium hydrocarbonate,** $RbHCO_3$, by evaporating over sulphuric acid, a soln. of rubidium carbonate in water sat. with carbon dioxide and in an atm. of carbon dioxide. Similar remarks apply to **cæsium hydrocarbonate,** $CsHCO_3$.

The **crystals** of sodium and potassium hydrocarbonates are monoclinic prisms. According to J. Schabus,[5] the crystals of sodium hydrocarbonate, $NaHCO_3$, have the axial ratios $a:b:c=0·7645:1:0·3582$, and $\beta=93°\ 19'$; and, according to H. J. Brooke, the crystals of potassium hydrocarbonate, $KHCO_3$, have $a:b:c=2·6770:1:1·3115$, and $\beta=103°\ 25'$. C. F. Rammelsberg, A. Levy, H. de Sénarmont, and H. St. C. Deville investigated the crystals of the last-named salt. W. C. Smith's value for the **specific gravity** of the sodium hydrocarbonate is 2·159; H. Buignet's, 2·163; F. Stolba's, 2·2208 (15°); H. G. F. Schröder's, 2·206; L. Playfair and J. P. Joule's, 2·192. W. C. Smith's value for the sp. gr. of potassium hydrocarbonate is 2·078; H. Buignet's, L. Playfair and J. P. Joule's, 2·092.

The dissociation press. of the alkali hydrocarbonates at different temp. have been previously discussed, and the results show the increasing stability of these salts as the at. wt. increase in magnitude.

W. E. Müller[6] gives the **heat of formation** of lithium hydrocarbonate as $2LiOH_{aq}+2CO_{2aq}=2LiHCO_{3aq}+22·1$ Cals. The heat of formation of sodium hydrocarbonate from its elements is given by J. Thomsen as 229·3 Cals.; by M. Berthelot as 227·0 Cals.; and by R. de Forcrand, 228·38 Cals.; for potassium hydrocarbonate M. Berthelot gives 230·4 and 233·3 Cals.; and R. de Forcrand, 231·63 Cals. R. de Forcrand gives for rubidium hydrocarbonate, 231·92 Cals.; and for cæsium hydrocarbonate, 232·93 Cals. M. Berthelot also gives for the **heat of neutralization**: $2NaOH_{aq}+2CO_{2aq}=2NaHCO_{3aq}+8·54$ Cals. at 15°; $2KOH_{aq}+2CO_{2aq}=2KHCO_{3aq}+22·0$ Cals.; and $K_2CO_{3aq}+CO_{2aq}=2KHCO_{2aq}+1·8$ Cals. For the **heat of solution** of potassium hydrocarbonate, M. Berthelot gives −5·3 Cals.

For the **heat of dissociation,** Q, of sodium hydrogen carbonate calculated from the vap. press., R. M. Caven and H. J. S. Sand give 30·7 Cals., and from R. de Forcrand's thermochemical data, 29·7 Cals. In the former calculation, $\log p = a - b/T$, and $Q = \log_e 10 = 2·30$, and $R = 2$ cals. The values of a and b are indicated previously. In the second calculation for sodium hydrocarbonate, the values $\{NaHCO_3\} = 228·38$ Cals.; $[Na_2CO_3] = 271·97$ Cals.; $\{H_2O\} = 58·06$ Cals.; and $\{CO_2\} - 97$ Cals. are substituted in $2[NaHCO_3] = [Na_2CO_3] + \{H_2O\} + \{CO_2\} - Q$. Similarly for potassium hydrocarbonate, the corresponding values are respectively 31·46 Cals. and 32·83 Cals.; for rubidium hydrocarbonate respectively 39·56 Cals. and 33·8 Cals., and for cæsium hydrocarbonate respectively 59·96 Cals. and 36·26 Cals. The discrepancy in the results of the calculations by the two methods is probably in part due to wrong values for the observed heats of formation of the compounds in question from the elements.

The **solubility** of sodium hydrocarbonate in water was measured by T. Bergmann, V. Rose,[7] J. Anthon, and A. B. Poggiale. The last-named worked between 0° and 70°, and H. C. Dibbits has shown that sodium hydrocarbonate cannot exist at 70° under the conditions of A. B. Poggiale's experiments. H. C. Dibbits' numbers about 20° agree with those of A. B. Poggiale, but below that temp. H. C. Dibbits' numbers are the smaller, and above that temp. the higher. H. C. Dibbits alone took special precautions against losses of carbon dioxide, for, as previously indicated, the soln. are stable only in the presence of an excess of carbon dioxide. J. Anthon, A. B. Poggiale, and H. C. Dibbits have also measured the solubility of potassium hydrocarbonate under similar conditions. The last named gives for 100 parts of water:

	0°	5°	10°	20°	25°	30°	40°	50°	60°
$NaHCO_3$ . . .	6·90	7·45	8·15	9·60	10·35	11·10	12·7	14·45	16·40
$KHCO_3$ . . .	22·05	25·0	27·7	33·2	36·1	39·0	45·3	49·9	60·0

F. Stolba says a sat. soln. of sodium hydrocarbonate at 16° has a sp. gr. 1·06904. According to J. Anthon, 100 parts of water at 11·25° dissolve 8·27 parts of sodium hydrocarbonate, forming a soln. of sp. gr. 1·0613; and likewise potassium hydrocarbonate at 11·2° dissolves 26·1 parts of the salt, and the soln. has a sp. gr. 1·1536. R. Engel found a sat. soln. of potassium hydrocarbonate at 0° has 23 grms. of salt per 100 grms. of water, and the sp. gr. is 1·127. F. Fouqué found a soln. of 1·15 grms. of potassium hydrocarbonate in 100 grms. of water had a sp. gr. 1·0074 (6°), and 1·0062 (19°), and a soln. of 3·54 grms. per 100 grms. of water, 1·0233 (0)° and 1·0216 (19°); F. Kohlrausch gives for soln. of 5·26 and 11·1 grms. of the same salt per 100 grms. of water at 15°, 1·0328 and 1·0674 respectively. W. H. Balmain found the solubility of sodium hydrocarbonate in water at 15° to be lowered by the presence of sodium chloride or sulphate; and the effect of sodium chloride or ammonium hydrocarbonate on the solubility of sodium hydrocarbonate in soln. sat.

TABLE LIII.—EFFECT OF SODIUM CHLORIDE AND AMMONIUM HYDROCARBONATE ON THE SOLUBILITY OF SODIUM HYDROCARBONATE.

Ammonium hydrocarbonate.						Sodium chloride.							
0°		15°		30°		0°		15°		30°		45°	
NH_4HCO_3	$NaHCO_3$	NH_4HCO_3	$NaHCO_3$	NH_4HCO_3	$NaHCO_3$	NaCl	$NaHCO_3$	NaCl	$NaHCO_3$	NaCl	$NaHCl_3$	NaC'	NaH(
0	0·82	0	1·05	0	1·65	0	0·82	0	1·05	0	1·31	0	1·6
1·39	0·58	2·16	0·71	2·91	0·83	6·0	0·09	6·06	0·12	6·12	0·17	6·18	0·2

with carbon dioxide has been measured by K. Reich, G. Bödlander and P. Breull, and by P. P. Fedotieff. Expressing the results in mols. of salt per 1000 grms. of water, R. Engel showed that the solubility of potassium hydrocarbonate in soln.

of normal potassium carbonate at 0° is lowered almost to zero with 81·4 per cent. of the normal carbonate. The addition of potassium hydrocarbonate to a sat. soln. of the sodium salt precipitates some of the latter. J. Anthon reported 100 parts of water between 10° and 11·2° when sat. with potassium hydrocarbonate contains 26·1 grms. of the salt, and it can then take up 6·0 grms. of sodium hydrocarbonate; similarly, if sat. with the sodium salt it contains 8·7 grms. $NaHCO_3$, and can then dissolve 19·3 grms. of potassium hydrocarbonate. There is nothing here to show that the soln. were in equilibrium with the solid phases. *Alcohol* lowers the solubility of sodium hydrocarbonate. According to F. Stolba, 100 grms. of alcohol of sp. gr. 0·941 dissolve 1·2 grms. of the salt at 15·5°; potassium hydrocarbonate is very sparingly soluble in alcohol. C. L. Berthollet says that 100 parts of hot alcohol dissolve 0·83 part of the salt. A. Vogel found 100 grms. of *glycerol* at 15·5° dissolve 8 grms. of sodium hydrocarbonate.

P. A. Favre and F. Roche found that on electrolyzing soln. of sodium hydrocarbonate, a mixture of oxygen and carbon dioxide was formed at the anode. F. Kohlrausch has measured the sp. conductivity of soln. of potassium hydrocarbonate at 18°. F. P. Treadwell and M. Reuter measured the mol. conductivity, μ, of soln. of a mol. in 256, 512, 1024, and 2048 litres of water at 18°, and found that μ is respectively 90·3, 92·1, 93·7, and 96·0. F. Kohlrausch [8] also measured the temp. coeff. of the conductivity. J. Kendall measured the eq. conductivity of soln. of sodium hydrocarbonate. G. Bödlander and P. Breull found the electromotive force of the cell $Pt|H_2$, CO_2, HCl, NaCl|NaCl, $NaHCO_3$, CO_2, H_2Pt at 20° with sat. soln.: 0·12*N*-HCl and the press. of the carbon dioxide 0·5 atm. The potential difference was 0·3985 volt. From the thermal value of the reaction: $NaCl+CO_2+H_2O=NaHCO_3+HCl$, the free energy of the reaction between hydrochloric acid and the hydrocarbonate is 8·7 and 9·1 cals. It is also shown that in order to form enough sodium hydrocarbonate to form a sat. soln. it would be necessary to pass carbon dioxide at the unattainable press. of $3·3\times10^6$ atm. into the soln. of sodium chloride. G. Meslin says sodium and potassium hydrocarbonate are diamagnetic.

The stability of dry and moist hydrocarbonates in air and of the aq. soln. has been previously discussed. Similar remarks apply to the action of heat on the salts. V. Rose reported, in 1801, that sodium hydrocarbonate has an alkaline taste; it does not change the colour of turmeric or litmus, but it turns logwood and red litmus blue; and colours syrup of violets green. If quite free from the carbonate, it is neutral to phenolphthalein at 0°; but F. W. Küster and F. P. Treadwell and M. Reuter found the soln. reddens phenolphthalein red at ordinary temp. The coloration with phenolphthalein will be very faint at 15° if the normal carbonate be absent. L. Cailletet [9] prepared a compound of liquid carbon dioxide and potassium carbonate which has been regarded as *bicarbonate de potassium anhydre*, $K_2C_2O_5$. P. Kasanezky found that hydrogen peroxide drives carbon dioxide from sodium or potassium hydrocarbonate and then reacts with the resulting carbonate forming a percarbonate. A double salt of sodium carbonate and hydrocarbonate occurs in Venezuela as *urao*, and in Egypt as *trona*. Analyses [10] of the Egyptian trona have been given by T. Remy, O. Popp, V. S. Bryant, M. H. Klaproth, J. Joffre, and A. Laugier; of Indian trona, by W. Wallace, D. Hooper, and W. H. Bradley and R. Reynolds; of Australian, by R. Daintree; of Venezuelan, by M. de Rivero and J. B. J. D. Boussingault; and of North American, by J. D. Weeks, and T. M. Chatard. The analyses of the natural deposits show that the salt is a mixture or compound of sodium carbonate and hydrocarbonate. M. H. Klaproth, O. Popp, and J. W. Döbereiner favour $Na_2CO_3.2NaHCO_3.3H_2O$, or $2Na_2O.3CO_2.4H_2O$. C. F. Rammelsberg's formula—$2Na_2CO_3.H_2CO_3.2$–$4H_2O$, that is, $Na_2CO_3.2NaHCO_3.2$–$4H_2O$—calculated from L. Pfeiffer's analyses of Indian trona, is in agreement with this conclusion. On the other hand, A. Laurent calculated the formula $Na_2CO_3.NaHCO_3.2H_2O$, or $3Na_2O.4CO_2.5H_2O$, from M. de Rivero and J. B. J. D. Boussingault's analyses of Venezuelan urao; R. Hermann,

R. Phillips, H. Rose, and J. W. Döbereiner believed that they had prepared the compound $Na_2CO_3.2NaHCO_3$, that is, $2Na_2O.3CO_2.H_2O$—which was called **sodium sesquicarbonate**—by crystallization during the cooling of a boiling aq. soln. of the hydrocarbonate; by evaporating a soln. of the hydrocarbonate in vacuo; by crystallization from a hot soln. of the component salts; or by melting together eq. proportions of the two salts, and exposing the product in a cellar for some weeks. C. Winkler poured 1920 parts of alcohol on top of a soln. made by dissolving 100 parts of the normal carbonate and 152 parts of the hydrocarbonate in 1920 parts of water. Acicular crystals of the alleged sesquicarbonate appeared in a few days at the surface of separation of the two liquids. Crystals of the normal carbonate with a crust of hydrocarbonate were formed at the bottom of the soln. These crystals were studied by A. B. Poggiale, and R. Schindler.

Later investigations by E. de Mondésir, V. von Zepharovich, T. M. Chatard, M. Soury, H. Lescœur, and J. Habermann and A. Kurtenacker favour the view that A. Laurent's formula, $Na_2CO_3.NaHCO_3.2H_2O$, represents the composition of the double salt. Crystals of this salt were made by P. de Mondésir by the following process:

Gradually add an intimate mixture of 8 parts of sodium hydrocarbonate and 28 parts of the decahydrated carbonate to a nearly boiling soln. containing 28 parts each of sodium chloride and decahydrated sodium carbonate in 100 parts of water making good the evaporation losses by more water. When all is dissolved the liquid is cooled slowly not lower than 20°. The double salt separates in fine needles which are separated from the mother liquor by decantation and suction. When washed with water, the crystals decompose, the normal carbonate passes into soln. leaving behind most of the hydrocarbonate. P. de Mondésir adds that the salt is very stable in sat. soln. of sodium chloride, probably because it is only slightly soluble even when heated, and even on boiling it loses its acid with excessive slowness. Nevertheless, a certain excess of the normal carbonate is necessary for its preservation. T. M. Chatard employed a somewhat similar process.

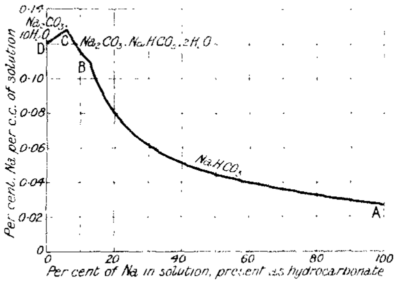

FIG. 73.—Conditions of Equilibrium of Sodium Sesquicarbonate.

J. J. Watts and W. A. Richards patented the preparation of this salt by removing the proper quantity of carbon dioxide from sodium hydrocarbonate by adding sodium hydroxide, sodium carbonate, or the hydroxides of the alkaline earths, and crystallizing the soln. at about 35°; C. Winkler obtained it from carbonated liquor of the ammonia-soda process; and T. M. Chatard by the spontaneous evaporation of soln. of normal sodium carbonate which had been exposed to the air some time and thereby absorbed carbon dioxide. There is a fairly general agreement that a temp. below 35° is not favourable to the formation of trona; and that the crystals develop better in sodium chloride soln.; and excess of the normal carbonate also favours the formation of trona. J. J. Watts and W. A. Richards say that if an excess of the hydrocarbonate be used, it crystallizes out unchanged. T. M. Chatard studied the influence of the composition of the soln. on the formation of trona, and obtained the results indicated in Table LIV with soln. containing a mol. of the normal carbonate. H. N. McCoy and C. D. Test have studied the conditions under which the sesquicarbonate is formed, and their results are summarized in Fig. 73.

The point *A* represents the solubility of sodium hydrocarbonate in water, the curve *AB*, the solubility curve of soln. containing increasing proportions of the normal carbonate in equilibrium with the hydrocarbonate as solid phase; at *B*, 12·9 per cent. of the sodium in the soln. is in the form of hydrocarbonate, and 87·1 per cent. in the form of sesquicarbonate. The curve *BC* represents the solubility with needle-like crystals of the sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$, as solid phase; and *CD*, with $Na_2CO_3.10H_2O$ as solid phase. The points *B* and *C* represent four-phase systems. *M. P. Appleby and K. W. Lane did not find the trona region at 18°.*

TABLE LIV.

Mols. $NaHCO_3$	Product—T = trona.			
	0·125	0·25	0·5	1·0
NaCl 0·5 . .	—	$T+Na_2CO_3.H_2O$	—	—
NaCl 1·0 . .	$T+Na_2CO_3.H_2O$	$T+NaHCO_3$	$NaHCO_3$	$NaHCO_3$
NaCl 2·0 . .	T	T	$NaHCO_3$	$NaHCO_3$

P. de Mondésir showed that the product is the same as J. B. J. D. Boussingault's urao, and he calls it *carbonate quatretiers*, or four-thirds carbonate, from the ratio $Na_2O : CO_2 = 3 : 4$, or $1 : \frac{4}{3}$. Hence, it can be called *sodium tetra-trita-carbonate*, or *tetrita-carbonate*; it is also **sodium monohydro-dicarbonate,** $Na_2CO_3.NaHCO_3.2H_2O$. M. Soury could find no evidence of any other in his measurements of the vap. press. of soln. of these two salts. V. von Zepharovich and M. T. Chatard adopt the view that *all native trona or urao deposits which have a different composition from the tetratrita-carbonate are mixtures of this carbonate with other sodium carbonates. The ideal* trona or urao corresponds with the formula of A. Lauren. This conclusion is supported by B. Reinitzer's, and W. Wallace's analyses as well as others previously mentioned.

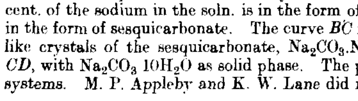

FIG. 74.—Crystals of Sodium Dihydrated Monohydro-dicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$.

The crystals of dihydrated sodium monohydro-dicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$—ideal trona or urao—are in the form of monoclinic prisms, Fig. 74. According to E. F. Ayres, the axial ratios are $a : b : c = 2·8426 : 1 : 2·9494$ and $\beta = 103° 29'$ in agreement with the measurements of V. von Zepharovich. W. Haidinger's value for the sp. gr. is 2·112; B. Reinitzer's, 2·14; and T. M. Chatard's, 2·1473 (21·7°). W. Haidinger gives the hardness between 2·5 and 2·75; and M. de Rivero and J. B. J. D. Boussingault under 3. W. Haidinger says the compound is less soluble in water than sodium carbonate. Solubility determinations have been made by A. B. Poggiale, who found for 100 grms. of water:

	0°	20°	30°	40°	60°	80°	100°
Gram-eq. Na . .	0·187	0·286	0·330	0·374	0·464	0·559	0·650

It is a little uncertain what is the solid phase in equilibrium with the soln. at the lower temp. As was shown by P. de Mondésir, H. Rose, and R. Schindler, trona is decomposed by recrystallization from water, by evaporating the soln., or by washing with water. *W. Haidinger found the crystals do not effloresce in air,* nor when confined over quicklime. H. Lescœur also observed no dissociation of the salt at ordinary temp., but E. F. Ayres says the crystals lose their lustre when exposed to air.

C. L. Berthollet, and J. J. Berzelius [11] found that when an aq. soln. of potassium hydrocarbonate is boiled, and then cooled, crystals of **potassium sesquicarbonate**

are formed; and that a similar result is obtained by cooling a soln. of equi-molecular proportions of potassium carbonate and hydrocarbonate in hot water. The crystals are said to be deliquescent in air and insoluble in alcohol; but A. B. Poggiale has measured the solubility of the salt in water. L. Gmelin says that H. Rose's experiments on the action of hot water on potassium hydrocarbonate render the existence of this salt doubtful. C. F. Rammelsberg obtained some monoclinic prismatic crystals of a salt which corresponded with $K_2CO_3.2KHCO_3.3H_2O$ from a mineral waterworks, and which were obtained by evaporating a large quantity of hydrocarbonate. The axial ratios were $a:b:c=2·6635:1:1·2952$, and $\beta=104° 55'$. F. A. Flückiger found that white needle shaped crystals with the composition $K_2CO_3.2KHCO_3.5H_2O$ were formed as an efflorescent incrustation on an earthenware vessel which had been used as a receptacle for potash, and which had been washed out and exposed to the sun. Attempts to prepare the salt artificially were not successful. There is room for doubting the existence of these salts as chemical individuals until the systems have been explored by the aid of the phase rule; M. P. Appleby and K. W. Lane found clear evidence of $K_2CO_3.2KHCO_3.3H_2O$ on the solubility curve, but they did not prepare it synthetically. It is stable only in contact with a very limited range of soln. approximating 825·8 grms. K_2CO_3 and 33·1 grms. $KHCO_3$ per litre. A. Baner has reported the formation of this double salt.

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§ 33. The Ammonium Carbonates

H. Kopp [1] said that he was unable to find any references to ammonium carbonate earlier than Geber's *Testamentum*, where it is possible that this salt was in question when it was said that the incineration *ex omnibus rebus etiam ex animalibus, piscibus, et volatilibus, potest fieri sal.* The first definite allusion to ammonium carbonate occurs in a work attributed, probably wrongly, to Raymund Lully—namely, the *Experimenta*, supposed by the scholars to have been written in 1330, whereas Raymund Lully died 1315. Here it was said that the urine of boys between eight and twelve years of age should be allowed to putrefy, and then distilled. The distillation should be repeated many times on the first fractions of each distillate. Finally, a salt was said to be obtained which is very volatile—it was called *mercurius animalis* or *spiritus animalis*. This same *sal volatile* was mentioned by many of the succeeding alchemists—*e.g.* J. von Roquetaillade refers to its formation by heating animal matters in a closed vessel: I. Hollandus called it *spiritus urinæ;* Basil Valentine called it *spiritus salis urinæ;* A. Sala noted that the spirit of urine can sat. (neutralize) the acids; J. B. van Helmont called it *spiritus salis lotii* or *spiritus salis cruoris;* J. R. Glauber called it *spiritus urinæ* and *spiritus volatilis salis armoniaci;* O. Tachen prepared it in a purified condition by distilling sal ammoniac and calcium carbonate; R. Boyle, and also J. Mayow, prepared it from blood and from urine.

In the seventeenth century it was supposed that the products derived from different sources were different; and all kinds of extravagant recipes were given. One directed that "5 lbs. of the skulls of persons who had been hanged should be distilled with 2 lbs. of dried vipers, hartshorns, and ivory." It was extolled as

"a cure for epilepsy" and for "suppressing the vapours that arise from stomach and spleen." The so-called *English drops* in the pharmacopœia of the seventeenth century were nothing more than *sal volatile* mixed with an ethereal oil, and sold at high prices because it was said to have been prepared by the destructive distillation of silk. R. Dossie maintained, in 1758, that the volatile alkali obtained from different sources had the same efficacy. When the alkaline character of *spiritus urinæ*, indicated by A. Sala, had been established, the product was called *alcali volatile salis ammoniaci*, and this was further abbreviated to *ammoniacum*, and finally to *ammonium*. The commercial carbonate of ammonia is the so-called *sal volatile, spirit of hartshorn*, or *sal volatile cornu cervi*, and it is a mixture of several ammonium carbonates.

C. Clemm and E. Erlenmeyer reported finding 0·03878 grm. of ammonium carbonate, and 0·682 grm. of carbon dioxide per 1000 litres of the air of stables. P. Schirlitz[2] also found ammonium carbonate in sea-water. A. Ladureau noted the formation of ammonium carbonate from the fermentation of the urea contained in urine. Ammonium acid carbonate or hydrocarbonate occurs as a mineral *teschemacherite* named after E. T. Teschemacher, who found it on the guano deposits of the islands off Patagonia; T. L. Phipson and W. Wicke reported it in the guano from the Chincha Islands; C. Wurster and A. Schmidt reported its presence in urine. Several observers—A. Schrötter, F. Rüdorff, A. Vogel, P. Seidler, C. F. Wolfrum, etc.—have discussed its presence in the purifying plant, mains, and gas-liquor associated with the manufacture of coal gas.

J. Black's investigation[3] of 1756 is the first contribution to the chemistry of the carbonates of ammonia, and he pointed out the chemical difference between the aqua ammonia and the solid carbonate of commerce. J. Priestley also, in 1774, dwelt on the same subject. T. Bergmann analysed the commercial carbonate in 1774; H. Davy emphasized the variable nature of the compounds of carbon dioxide and ammonia in 1799; while C. L. Berthollet (1806) and J. Dalton (1819) demonstrated that there are several different carbonates of ammonia. In his paper *On the combinations of carbonic anhydride with ammonia and water* (1870), E. Divers showed that there are at least three well-defined ammonium carbonates—the normal carbonate, the hydrocarbonate, and the sesquicarbonate. On the other hand, in his paper *Ueber die Verbindungen des Ammoniaks mit der Kohlensäure* (1839), H. Rose claimed to have shown that an indefinitely large number of these compounds can be prepared, and he described twelve of them. He said:

> Carbonic acid and ammonia can unite in the most varied proportions. The number of these combinations is indeed surprising. I have prepared several of them . . . and it would have been easy for me to have increased their number . . . but I have contented myself with indicating the possibility of their existence since their preparation and examination would occasion more trouble than the subject merited. . . . The reason for the great number of these combinations arises less from the weak affinity which carbonic acid has for ammonia, than from the circumstances that the various combinations have a great tendency to form double salts with one another. *I regard the several salts which carbonic acid forms with ammonia as double salts combined in different proportions.*

It is now thought that most of H. Rose's carbonates were really mixtures, and that E. Divers' list includes those whose individuality has been satisfactorily established. The ammonium normal and hydrocarbonates are usually regarded respectively as the secondary and primary salts of dibasic carbonic acid:

$$\begin{matrix}HO \\ HO\end{matrix}\!>\!C{=}O \qquad \begin{matrix}NH_4O \\ HO\end{matrix}\!>\!C{=}O \qquad \begin{matrix}NH_4O \\ NH_4O\end{matrix}\!>\!C{=}O$$

Metacarbonic acid — Ammonium hydrocarbonate — Ammonium normal carbonate

the sesqui-carbonate is considered to be a double salt of these two carbonates, namely, $2(NH_4)HCO_3.(NH_4)_2CO_3$. If carbonic acid be tetrabasic, then these compounds will be meta-carbonates. It will be observed that with the exception of the hydrocarbonate, these salts have not been obtained anhydrous, they are always

hydrated—$(NH_4)_2CO_3.H_2O$, and $2(NH_4)HCO_3.(NH_4)_2CO_3.H_2O$. E. Divers believes that they are salts of a tetrabasic acid :

$\begin{matrix}HO\\HO\end{matrix}>C<\begin{matrix}OH\\OH\end{matrix}$	$\begin{matrix}NH_4O\\NH_4O\end{matrix}>C<\begin{matrix}OH\\OH\end{matrix}$	$\begin{matrix}NH_4O\\NH_4O\end{matrix}>C<\begin{matrix}ONH_4\\ONH_4\end{matrix}$
Orthocarbonic acid, H_4CO_4	Secondary ammonium orthocarbonate, $(NH_4)_2H_2CO_4$, *i.e.* $(NH_4)_2CO_3.H_2O$	Normal ammonium orthocarbonate, $(NH_4)_4CO_4$

This would make the sesqui-carbonate $2(NH_4)HCO_3.(NH_4)_2H_2CO_4$. E. Divers says that evidence of the probable existence of a normal ammonium orthocarbonate is not altogether wanting in that J. Davy, by treating the commercial carbonate with aq. alcohol, obtained undissolved hydrocarbonate and a soln. of ammonia and carbon dioxide eq. to ammonium hydroxide and the normal metacarbonate. Similarly, when aq. alcohol acts on an aq. soln. of the commercial or normal carbonate, the hydrocarbonate is precipitated, and there remains a soln. which is more alkaline than that of the normal metacarbonate. Further, when potassium carbonate is distilled with its eq. or more than its eq. of ammonium chloride and aq. alcohol, the first portion of the distillate is a soln. of the normal metacarbonate, or one eq. to it, and it separates into a more basic soln. and crystals of the sesqui- and hydro-carbonates. When water is repeatedly treated with fresh quantities of the commercial carbonate, and one or two crops of crystals of sesqui-metacarbonate have been obtained, the mother liquor contains a little more than two eq. of ammonia to one of carbon dioxide. Hence, added E. Divers, it seems less probable to assume that a soln. of the normal metacarbonate separates into the sesqui- or hydro-carbonate and ammonium hydroxide than into one of these salts and the normal orthocarbonate : $4CO(ONH_4)_2H_2O=2(NH_4O)_2C(OH)_2+(NH_4)_4H_2(CO_3)_3+2H_2O$.

The preparation of normal ammonium carbonate, $(NH_4)_2CO_3$.—Before J. J. Berzelius had published his ammonium theory, the compound formed by the union of ammonia and carbon dioxide was thought to represent the normal carbonate. It was then recognized that this is not the required ammonium carbonate, $(NH_4)_2CO_3$, but is another compound altogether, *viz.* $CO_2(NH_3)_2$, to which the term ammonium carbonate was applied. In 1789, however, A. F. de Fourcroy and C. F. Bucholz [4] prepared the crystalline double salt of magnesium carbonate with normal ammonium carbonate, $(NH_4)_2CO_3.MgCO_3.4H_2O$. As a result of his attempt to make the normal carbonate, H. Rose wrote : "The neutral anhydrous ammonium carbonate cannot be obtained with the amount of water necessary to convert the ammonia into oxide of ammonium: $(NH_3)_2H_2OCO_2$, *i.e.* $(NH_4)_2CO_3$." H. St. C. Deville also succeeded in preparing only the two crystalline carbonates—*viz.* the sesquicarbonate and the acid carbonate.

In 1806, C. L. Berthollet probably obtained a weak soln. of normal ammonium carbonate, $(NH_4)_2CO_3$, by distilling a soln. of the acid carbonate, but, in 1813, J. Dalton first described a solid carbonate neutral in composition containing two mols. of ammonia to one of carbon dioxide. It also contained a mol. of water, *i.e.*, $CO_2H_2O(NH_3)_2$. J. Dalton prepared the normal carbonate in two ways : (1) By distilling the commercial carbonate and collecting the first product of the distillation before it had been exposed to the air ; (2) By adding sufficient ammonia to a warm sat. soln. of the commercial carbonate, to raise the proportion to such a degree that when cooled, the normal carbonate was precipitated ; and (3) by leaching the commercial carbonate with an insufficient amount of water to dissolve the whole, a soln. is obtained containing a greater proportion of ammonia than is present in the commercial salt. This observation was later on (1838) confirmed by R. Scanlan. The fractional soln. of the normal carbonate is determined by its greater solubility. H. Davy (1799) had previously prepared what he regarded as the most ammoniacal carbonate by the first of these methods, but gave no analyses, and J. Davy repeated his brother's experiments and found the product to be a hydrated compound containing two eq. of ammonia to one of carbon dioxide.

Meanwhile, T. Thomson stated that the normal carbonate could be made by mixing carbon dioxide with twice its volume of ammonia and an equal volume of water vapour. Although J. Davy confirmed this statement, it is very doubtful whether the product of this reaction is a single substance, but it is more likely to be a mixture. L. Hünefeld prepared a neutral combination of ammonia and carbon dioxide by distilling the commercial carbonate with aq. alcohol, but he did not determine the degree of hydration. H. Rose also prepared the more volatile portion of the first product of the slow distillation of the commercial carbonate, and found it to contain two eq. of ammonia to one of carbon dioxide, and there was associated with it half an eq. of water, making $(CO_2)_2H_2O(NH_3)_4$, so that it is doubtful if this can be regarded as a true ammonium caroonate. H. Rose also obtained the same compound by distilling a mixture of ammonium chloride and sodium carbonate. In 1870, E. Divers pointed out that all the methods available for the preparation of normal *ammonium carbonate* depend for their success on the hydration of the carbamate, the combination of ammonia and water with the acid or half-acid carbonate, or on both these actions. Nearly all the methods of preparation depend upon the low solubility of ammonium carbonate in aq. ammonia, or in alcoholic soln.

(1) The pulverized commercial carbonate is digested in a closed flask with conc. aq. ammonia below 12°, in about 2 hrs. a mealy crystallized mass of crystals will remain. These are dried by press. between folds of filter paper. Care is to be taken to expose the product as little as possible to the free action of atm. air. (2) In another process, any one of the ammonium carbonates is digested in a closed flask with four times its weight of conc. aqua ammonia between 20° and 25°, until it is dissolved. About 2 days are usually required. The soln. is left in a cool place with the vessel not completely closed so that some ammonia can escape. Small interlacing standard prismatic crystals appear. If too little ammonia be used, crystals of what are probably ammonium carbonate are formed, while if too much ammonia be present the crystals separate slowly and with difficulty. The crystals are separated and dried as before. This process is more manageable than the first process. (3) If ammonia gas be passed into a conc. soln. of the commercial carbonate, crystals of ammonium carbonate may separate while the gases are passing if the soln. be kept cool, or afterwards if the soln. be kept in a closed vessel in a cool place. (4) One of the best modes of preparation is to dissolve the commercial carbonate in a warm dil. soln. of ammonia in a closed or nearly closed vessel. On cooling the soln., crystals of the normal carbonate are formed—the crystals are small if a large proportion of free ammonia be present; and if too little ammonia be present, the half-acid carbonate is formed. (5) Normal ammonium carbonate slowly crystallizes from a soln. of commercial carbonate in aq. ammonia to which dil. alcohol has been added in quantity just insufficient for precipitation. The size of the crystals is smaller in proportion as the quantity of free ammonia predominates. If an excess of alcohol is added, the whole may form a mushy mass of crystals. (6) On cooling a soln. of ammonium carbamate in water at 30°–35°, in a closed vessel, a little normal ammonium carbonate crystallizes out. (7) A soln. of ammonium carbamate in conc. aq. ammonia in a closed vessel at ordinary temp. deposits crystals of the normal carbonate when set aside with the vessel imperfectly closed. (8) The action of carbon dioxide on conc. aqua ammonia so as to leave the ammonia in excess, furnishes a soln. which when allowed to stand in a closed vessel, deposits crystals of the normal carbonate. (9) Large crystals are obtained by dissolving the commercial carbonate in water at a gentle heat in a closed or nearly closed vessel, and allowing the soln. to cool and crystallize. The mother liquor is decanted on to a fresh quantity of the commercial carbonate and the processes of dissolution, cooling, crystallization, and decantation are repeated until the soln., after depositing a compact crop of thin plates, furnishes the half-acid- or sesqui-carbonate. The mother liquor remaining after standing one or two days will deposit large prismatic crystals of the normal carbonate on standing in a closed vessel in a cool place. Instead of waiting for the soln. to crystallize, it can be treated with ammonia water when minute crystals of the required salt are deposited.

E. Divers also prepared a little of the normal carbonate by J. Dalton's wet method; and found that the distillation method also gives the normal carbonate in the form of long fibrous prisms which appear on the condensing surface at the beginning of the distillation. These same crystals readily change into the acid carbonate. The same crystals or the remains of their decomposition are often seen on the sides of bottles containing freshly prepared commercial carbonate; similar crystals are

obtained by raising the temp. of a soln. of the normal carbonate contained in a retort or flask with the neck closed sufficiently to prevent diffusion. The drops of moisture which first condense on the neck, soon form fibrous prismatic crystals whose analyses agree with those of the normal carbonate. These crystals are not a true product of the distillation process since, when they are forming, the carbonate in the retort has not reached the temp. required for the vaporization. J. E. Marsh and R. de J. F. Struthers prepared this salt by heating ammonium oxalate or mercuric cyanide with water in a sealed tube: $HgCy_2+4H_2O=Hg+CO+(NH_4)_2CO_3$: M. Lorin, by heating the ammonium tartrate to 400°. other products were simultaneously formed; R. Phillips, by distilling a mixture of ammonium chloride, potassium carbonate, and alcohol; and O. Angelucci, by the action of acetylene on nitric oxide at a high temp. The same salt can be obtained by distilling gas liquor over *calcium carbonate, for under these conditions, P. Seidler says that with the excep*tion of a little ammonium sulphide virtually all the ammonia is obtained in the form of the normal carbonate.

The properties of normal ammonium carbonate.—Monohydrated ammonium *carbonate forms elongated plates or flattened prisms,* which *smell of ammonia,* and is presumably a product of the decomposition of the normal carbonate; the pungent taste also affects the tongue as a caustic. The crystals were analyzed by J. Dalton, who found the composition to be very nearly that required for $(NH_4)_2CO_3.H_2O$, *the products of all the different methods of preparation indicated by E. Divers* have the same composition. E. Divers found that when exposed to air, the crystals become moist and opaque, lose ammonia and water, and form ammonium hydrocarbonate: $(NH_4)_2CO_3.H_2O=NH_4HCO_3+H_2O+NH_3$. The salt thus becomes wet in a stoppered bottle. The salt decomposes at 58°, forming water, ammonia, and carbon dioxide: $(NH_4)_2CO_3.H_2O=CO_2+2H_2O+2NH_3$. When heated slowly on a water-bath in a retort with its neck dipping under mercury, between 49° and 50°, drops of liquid collect in the neck, and these form fibrous crystals of the normal carbonate, $(NH_4)_2CO_3.H_2O$, as indicated above; no marked change occurs until, between 58° and 60°, when a moist solid distillate is formed, and the contents of the retort gradually liquefy. The proportion of $NH_4:CO_2$ in both the residual liquid and the distillate is that required for the normal carbonate, but the distillate has too little water for the normal carbonate, the residue in the retort gives crystals of the normal carbonate. When the normal carbonate is distilled slowly enough, E. Divers found that the products are ammonium carbamate and water, but when distilled faster, then the whole of the products of distillation can condense in the receiver, only partial condensation occurs in such a way that the commercial carbonate, $(CO_2)_2H_2O(NH_3)_3$, is formed: $2\{(NH_4)_2CO_3.H_2O\}=(CO_2)_2H_2O(NH_3)_3+3H_2O+NH_3$. P. A. Favre and C. A. Valson [5] give 16·946 Cals. for the heat of formation: $2NH_{3soln.}+CO_{2gas}=(NH_4)_2CO_{3soln.}$; and M. Berthelot gives for the heat of decomposition 16·3 Cals.

E. Divers found normal ammonium carbonate is soluble in rather more than its own weight of water at 15°, and by cooling the soln. in a closed vessel, some of the original salt mixed with other carbonates crystallizes out again; the soln. may exhibit supersaturation phenomena, 100 grms. of glycerol dissolve 20 grms. of the normal carbonate at 15°. P. A. Favre and C. A. Valson found a 10·3 c.c. increase in volume attended the soln. of an eq. of the salt in a litre of water; and the sp. gr. of a N-soln. to be 1·0178. E. Divers said the sat. soln. has an oily consistency. J. L. M. Poiseuille found the velocity of flow of a soln. 1 : 1000, at 11·2°, to be 583·8 sec., and of a soln. 1 : 25, 602·9 sec. When the corresponding value for water is 575·6 sec., T. Graham found that in 8·08 days at 20·1°, the rates of diffusion of 1, 2, 4, and 8 per cent. soln. are respectively represented by 0·4478, 0·8845, 1·7496, and 3·2465 grms. The aq. soln., said E. Divers, smells strongly of ammonia, and if exposed to the air, it loses ammonia freely. When gradually heated, the aq. soln. begins to effervesce between 70° and 75°, and boils freely between 75° and 80°, yielding vapours which condense into a moist solid. When the soln. which has

been boiled is allowed to cool, it is found to be unchanged in properties, except that it is less conc. E. Drechsel showed that in aq. soln., the normal carbonate passes into the carbamate, and H. J. H. Fenton showed that a balanced reaction is involved: $NH_4O.CO.ONH_4 \rightleftharpoons NH_2.CO.ONH_4+H_2O$. The change proceeds in accordance with the law of mass action. The degree of hydrolysis of the carbamate is a *function* of the conc. of water, and minimum change occurs when equimolecular proportions of water and ammonium carbamate are present; the amount of hydrolysis is less, the lower the temp., so that at a low enough temp. the degree of hydrolysis will be *nil*; and, conversely, a low conc. of the water favours the formation of the carbamate. The reaction has also been studied by K. Buch, F. E. C. Scheffer, and J. J. R. McLeod and H. D. Haskins, who find that aq. soln. of the carbamate decompose until a state of equilibrium is established between the carbamate carbon dioxide and the total carbon dioxide, and the carbamate ammonia and the total ammonia. The equilibrium equations are: $NH_4O.CO.NH_2+H_2O \rightleftharpoons (NH_4)_2CO_3$; and $(NH_4)_2CO_3+H_2O \rightleftharpoons NH_4OH+NH_4HCO_3$. K. Buch found the relations indicated in Table LV, between the carbamate, hydrocarbonate, and free ammonia, in mols

TABLE LV.

Total concentration.		Carbamate.	Hydrocarbonate.	Total NH_3 in salts.
CO_2	NH_3			
1·066	2·132	0·424	0·642	1·490
0·533	1·066	0·174	0·369	0·697
0·278	0·556	0·070	0·208	0·348
0·107	0·214	0·016	0·091	0·123

per litre, where the conc. of the ammonia is equal to that of the hydrocarbonate. R. Wegscheider has also attempted to find the conc. of the various mol. and ionic species—NH_3, NH_4OH, CO_2, H_2CO_3, HCO_3', CO_3'', OH', $H^{\cdot}$, with undissociated water and salt. The solubility of certain carbonates in aq. soln. of ammonium carbonate may be due to the formation of complex carbonate ions, or complex ammino cations, to the transformation of carbonate into hydrocarbonate ions, or to the solvent action of hydroxyl ions. E. Terres and H. Weiser measured the partial press. of aq. soln. of ammonia and carbon dioxide between 20° and 80°. H. Kappeler investigated the electrolysis of soln. of ammonium carbonate.

E. Divers noted that the addition of conc. aqua ammonia or the passage of ammonia gas, precipitates normal ammonium carbonate unchanged from its aq. soln. Ammonium carbonate, indeed, is but sparingly soluble in aqua ammonia at low temp., the amount dissolved increases as the temp. rises. When crystals of ammonium carbonate are digested for two to three days with water sat. with ammonia, between 20° and 25°, they dissolve "in apparently unlimited quantity, and are changed into ammonium carbamate": $(NH_4)_2CO_3.H_2O=2H_2O+CO_2(NH_3)_2$. *No urea is formed. The presence of ammonia* therefore hinders the conversion of carbamate to carbonate, and favours the conversion of carbonate to carbamate; similarly, a high conc. of water mols. favours the hydrolytic conversion of carbamate to carbonate. J. J. R. McLeod and H. D. Haskins found that a soln. of ammonium carbamate in ice-cold water depresses the f.p. of water less than does the same soln. after standing a few minutes at room or body temp. This is accounted for by the conversion of carbamate (two ions) into ammonium carbonate (three ions).

M. Traube noted that hydrogen peroxide is formed during the slow oxidation of copper in the presence of ammonium carbonate. H. J. H. Fenton observed that when ammonium carbonate is treated with metallic sodium, cyanamide, $Cy.NH_2$, is formed by the loss of three mols. of water: $2(NH_4)_2CO_3+3Na_2=6NaOH+3H_2+2CyNH_2$. H. Delbrück investigated the action of potassium on the salt.

J. S. Muspratt, H. Rose, and H. Bley studied the action of ammonium carbonate on soln. of aluminium salts; C. Struckmann, on the alkali silicates; A. Müller, and P. P. Fedotieff, on potassium chloride in the presence of carbon dioxide; and P. Kasanetzky, on hydrogen peroxide whereby a percarbonate is formed. B. Gerdes obtained platinum bases during the electrolysis of soln. of ammonium carbonate with platinum electrodes, and in the electrolysis of soln. of the normal carbonate, F. Fichter and H. Kapeller found that ammonium nitrate and oxygen appear at the anode—no nitrite nor urea, $CO(NH_2)_2$, was detected. E. A. Werner and co-workers, T. B. Johnson, A. J. Hill and B. H. Bailey, A. Claus, J. Waddell, F. A. Gilfillan, and G. Inghilleri have studied the action of ammonium carbonate on carbon disulphide and obtained ammonium dithiocarbamate, $NH_2CS.S.NH_4$, at 100°–110°; ammonium thiocyanate, NH_4SCy, at 120°–130°; and thiourea, $CS(NH_2)_2$, at 160°.

E. Divers compared the action of ammonium carbonate and carbamate, and sodium carbonate on calcium chloride soln. When a dil. soln. of ammonium carbonate is added to an ammoniacal soln. of calcium chloride, with constant agitation, the gelatinous precipitate first formed redissolves, and when the soln. is allowed to stand, the precipitate gradually re-forms; with a larger proportion of ammonium carbonate, some of the precipitate first formed is permanent, and it is days before precipitation is so far complete that the supernatant liquor gives no further precipitate on boiling. The presence of ammonia also retards the precipitation of calcium carbonate in like manner when sodium carbonate is substituted for ammonium carbonate. E. Divers also says that normal ammonium carbonate appears to act on glass bottles and flasks in which the solid is stored for some time, for the transparency of the surface is destroyed; the action was not observed with soln. of the salt. W. Kowalewsky and M. Markewicz studied the physiological action of ammonium carbonate; A. Rössing used the salt in water analyses.

Ammonium sesquicarbonate, or half-acid-carbonate, $(NH_4)_4H_2(CO_3)_3.H_2O$, or $2NH_4HCO_3.(NH_4)_2CO_3.H_2O$.—H. Rose[6] first definitely prepared this salt in 1839, by distilling the commercial carbonate at a gentle heat in a retort with its mouth joined to a tube dipping under mercury, and arresting the operation as soon as the remaining contents of the retort had entirely liquefied. Crystals of the salt in question were obtained when the molten mass was allowed to crystallize. E. Divers heated to 60° in a retort the commercial carbonate just covered with water; when all was dissolved, the soln. was cooled, and a crop of crystals of the sesquicarbonate mixed with the hydrocarbonate was obtained. L. Hünefeld probably obtained crystals of this same salt, three years earlier than H. Rose, on cooling the aq. alcohol from which he had distilled some commercial carbonate, since the rhombic plates he obtained correspond with the rhombic plates of the sesquicarbonate which can be obtained by this very process. H. St. C. Deville in his paper: *Sur la forme et la composition des carbonates ammoniacaux,* described the crystalline form of this salt which he prepared by dissolving the commercial carbonate at 30° in conc. aqua ammonia diluted with enough water to prevent its boiling at 30°, and setting aside the soln. to crystallize with or without the previous addition of alcohol. E. Divers has discussed the details required to ensure success; and he showed that the same salt can be obtained by the distillation of ammonium magnesium carbonate. The liquid distillate gives crystals of the sesquicarbonate, and the more remote parts of the solid in the neck of the retort also consist of the sesquicarbonate. E. Divers obtained the same salt by distilling potassium carbonate mixed with an eq. amount of ammonium chloride, along with aq. alcohol, according to the directions of the London Pharmacopœia for preparing *spiritus ammoniæ aromaticus.* The first fraction of the distillate deposits six-sided plates of the sesquicarbonate, along with a little hydrocarbonate, but the distillate as a whole is a soln. of the normal carbonate. T. J. Pelouze and E. Frémy stated that H. Rose's sesquicarbonate can be prepared by cooling an aq. soln. of the commercial carbonate at about 0°. E. Divers showed that this statement is erroneous since both he,

and H. St. C. Deville, obtained crystals of the hydrocarbonate under these conditions.

E. Divers says that ammonium sesquicarbonate forms "thin elongated six-sided plates, or, when the plates are left to grow in the mother liquor, flattened rectangular prisms terminated by the faces of a rhombic octahedron." The bipyramidal crystals belong to the rhombic system, and, according to H. St. C. Deville's measurements, have the axial ratios $a:b:c=0.6635:1:0.4585$. The solid has a very pungent ammoniacal taste and smell, but less so than the normal carbonate. The analyses of H. Rose were represented by the formula $(NH_3)_4(H_2O)_5(CO_2)_3$, or $(NH_4)_4H_2(CO_3)_3.2H_2O$. This formula was adopted by H. St. C. Deville, but E. Divers showed that Deville's analyses agree with $(NH_4)_4H_2(CO_3)_3.H_2O$, as do E. Divers' own analyses. Consequently, the latter is the result generally accepted. The sesquicarbonate, like the normal carbonate, changed into the hydrocarbonate on exposure to air: $(NH_4)_4H_2(CO_3)_3.H_2O=H_2O+NH_3+3(NH_4)HCO_3$. The difficulty of preventing this change explains the doubt respecting the accuracy of H. Rose's analyses. The apparent moisture of the exposed crystals is not due to the absorption of moisture from the air, but rather to the decomposition of the salt which is moistened with the product of its own decomposition from the crystals. The crystals melt when heated and are decomposed—a little water and three volumes of carbon dioxide with four of ammonia are first formed, then some more water and carbon dioxide are given off until what is virtually the normal carbonate remains in the retort. When the sesquicarbonate is distilled faster than the products can condense in the receiver, the commercial carbonate, $(CO_2)_2H_2O(NH_3)_3$, is formed: $3(NH_4)_4H_2(CO_3)_2.H_2O=4(CO_2)_2H_2O(NH_3)_3+8H_2O+CO_2$. At 15°, 100 parts of water dissolve rather less than 20 parts of the salt; if less water than this is used, the soln. becomes sat. and slowly decomposes the undissolved salt, leaving behind the hydrocarbonate. A soln. sat. at 20° evolves sufficient carbon dioxide to lift the stopper from the containing bottle, and when the soln. is heated it effervesces copiously. When the sat. soln. is cooled, it furnishes crystals of the hydrocarbonate. The sesquicarbonate is also decomposed by alcohol, and a residue of hydrocarbonate is left undissolved. In summing up the properties of the sesquicarbonate, E. Divers says that it seems to be intermediate in its chemical properties, as it is in composition to the normal- and hydrocarbonates. Ammonium sesquicarbonate acts on glass bottles like the normal carbonate does.

Ammonium hydrocarbonate, or ammonium acid carbonate, NH_4HCO_3.—In 1806, C. L. Berthollet[7] gave a clear account of the properties of the crystals of ammonium hydrocarbonate, acid carbonate, or bicarbonate, which he prepared by saturating a soln. of the sesquicarbonate with carbon dioxide. J. C. C. Schrader also prepared the same salt in a similar manner in 1803. J. Dalton (1813) also prepared this salt by exposing the commercial carbonate to the air, and he correctly analysed the product which he isolated. According to E. Divers, ammonium hydrocarbonate can be obtained: (1) by exposing the commercial carbonate, sesquicarbonate, normal carbonate, or carbamate to air; (2) by heating the commercial carbonate or sesquicarbonate with insufficient water to dissolve it—the normal carbonate under similar conditions also gives a little hydrocarbonate (J. Davy, H. Rose, H. Vogler); (3) by treating the commercial carbonate, sesquicarbonate, or normal carbonate with aq. alcohol (H. Rose, H. St. C. Deville); (4) by cooling a sufficiently conc. aq. soln. of the commercial carbonate or sesquicarbonate (H. Rose H. St. C. Deville); (5) by adding alcohol to an aq. soln. of the commercial carbonate the sesquicarbonate, or the normal carbonate (J. Davy, N. W. Fischer, H. St. C. Deville); (6) by treating an aq. soln. of the commercial carbonate, sesquicarbonate, or normal carbonate with carbon dioxide (J. Davy, P. Seidler, C. L. Berthollet, J. C. C. Schrader, H. St. C. Deville); and (7) by mixing together carbon dioxide, ammonia, and water vapour in equi-molecular proportions (T. Thomson); this process was patented by W. Gossage in 1854. A like result is obtained if an excess of carbon dioxide is used when the hydrocarbonate is probably the product

of the action of carbon dioxide and water on the ammonium carbonate first formed. The following is E. Divers' modification of T. Thomson's process:

Some acid ammonium carbonate in crystals, crushed small, and dried by exposure to the open air, or, better still, over sulphuric acid, is passed into a dry retort with a sufficiently long neck, or with its neck prolonged by a glass tube, which is better. The retort is placed in a water-bath, with its mouth or the open end of the tube prolonging the neck, as the case may be, dipping under mercury. The water-bath is then brought to the temp. of 62°, and not allowed to pass this. After a while no gas or air escapes through the mercury, if the heat be properly regulated; so that this fact serves, as well as the height of the thermometer, to indicate when the heat is getting too high. If the temp. be allowed to fall too much, the mercury rises in the tube. At first, liquid drops form on the neck of the retort, which gradually solidify into needle-like crystals. These again lose, more or less, their transparency; and then the process of formation of the deposit can no longer be followed. The hydrocarbonate forms in bulk at a distance of about 16 to 20 cm. along the neck from the body of the retort. The operation is a very slow one. When it is arrested the neck of the retort is cut off and broken up, the product chipped off from the fragments, and its purity ascertained by leaving it exposed for a time in dry air, when, if pure, it will retain the translucency it possesses. The outermost layer and some other parts of it will be sure to prove impure. If the hydrocarbonate is more rapidly converted into vapour, the process fails. When successfully carried on, if the process be arrested at any time, and the contents of the body of the retort examined, they will be found to be dry, unchanged hydrocarbonate, having only an evanescent odour of ammonia. In the other case the contents of the retort will be damp or wet, and much more ammoniacal.

R. Scanlan obtained the hydrocarbonate by subliming the normal carbonate—the lower part was hydrocarbonate, the upper part carbamate. P. R. de Lambilly, and A. Neuburger passed air and water vapour over white-hot coke, and removed the carbon monoxide from the mixture $N_2+3H_2+2CO_2+2H_2O=2NH_4HCO_3$. R. Phillips found the hydrocarbonate is sometimes produced in preparing the carbonate on a commercial scale.

In 1839, H. Rose claimed to have made ammonium hydrocarbonate in three different states of hydration, namely, NH_4HCO_3; $4(NH_4)HCO_3.H_2O$; and $2(NH_4)HCO_3.H_2O$. Before this, J. Davy prepared the salt in four different ways, and found the composition uniform, although H. Rose's method for $4(NH_4)HCO_3.H_2O$ was included in J. Davy's series; similar results were obtained by H. St. C. Deville. E. Divers also found that the crystals obtained by passing carbon dioxide into a soln. of the commercial carbonate are identical in form and appearance with those obtained by pouring hot water on the commercial carbonate which, according to H. Rose, should give $4(NH_4)HCO_3.H_2O$. The third salt, $2(NH_4)HCO_3.H_2O$, was prepared only once, and in small quantity. E. Divers could not verify H. Rose's preparation, and therefore wrote, "I am disposed to regard the existence of such a salt as extremely doubtful." Hence, the available evidence justifies the conclusion that only one definite ammonium hydrocarbonate has been prepared, and the analyses of J. Dalton, H. Rose, J. Davy, H. St. C. Deville, and E. Divers indicate that its formula is $(NH_4)HCO_3$.

The properties of ammonium hydrocarbonate.—Ammonium hydrocarbonate occurs in the form of a powder, in transparent or opalescent crystals, and in translucent crystalline masses. The crystals have been measured by H. Rose, W. H. Miller, H. St. C. Deville, C. F. Rammelsberg, F. Rüdorff, etc.; they belong to the rhombic system, and have the axial ratios $a:b:c=0·6726:1:0·3998$. H. Rose claimed to have once made monoclinic crystals of ammonium hydrocarbonate, isomorphous with the potassium salt, by evaporating a soln. of the normal salt in vacuo, but this observation has not been confirmed. In his 1852 paper, H. St. C. Deville stated that he believed that he had prepared crystals of the hydrocarbonate belonging to a different system to the ordinary salt, but in his 1854 paper he attributed little weight to this observation, and stated only one hydrocarbonate exists, but since the crystalline form of this salt is not isomorphous with the corresponding potassium hydrocarbonate, he stated that both these salts will prove one day to be dimorphous, implying that the unknown form of the one carbonate will prove to be isomorphous

with the known form of the other. Mixed crystals of the two salts have not yet been prepared.

H. Schiff[8] found the sp. gr. of the crystalline salt is 1·573; and G. J. Ulex that of the natural crystals, 1·45; G. J. Ulex gives 1·5 for the hardness. J. L. M. Poiseuille gives for the speed of flow of a soln. 1 : 100 at 11·2° through narrow tubes as 580·6 sec. when the value for water is 575·6 sec. H. C. Dibbits found the vap. press. of soln. sat. at 15°, 30°, 40°, and 50° to be respectively 120, 212, 356, and 563 mm. M. Berthelot and G. André's value for the heat of soln. of a mol. of the salt in 25 litres of water is −6·85 Cals., and M. Berthelot's value for 50 litres, −6·28 Cals.; and for the heat of dilution of a soln. $(NH_4)HCO_3+40H_2O$, with addition of 60, 160, and 360 mols. more of water, J. Thomsen found respectively −176, −288, and −384 cals. M. Berthelot and G. André found for the heat of formation $CO_{2aq}+NH_{3aq}=(NH_4)HCO_3$ in 20 litres of soln., 9·130 Cals.; 9·5 Cals. in 25 litres of soln.; and 9·73 Cals. in 2 litres of soln. The heat of formation from its elements is 205·3 Cals. A. des Cloizeaux, and V. von Lang found that the crystals have a negative double refraction, and that the indices of refraction are $\alpha=1·5227$; $\beta=1·5358$; and $\gamma=1·5545$.

As noticed by J. Dalton, ammonium hydrocarbonate is very slowly dissipated in moist air. According to J. Davy, it is decomposed by atm. moisture and rendered alkaline. H. C. Dibbits found that the dry solid decomposes at ordinary temp. into carbon dioxide, ammonia, and water, without alteration in the composition of the residue. H. Vogler found that 1·2 grms. in a watch glass over sulphuric acid and calcium hydroxide, under a bell-jar, lost 0·9 grm. in 7 days, it gradually lost in weight each day until in four weeks all had vanished. According to M. Meslens, the volatilization is much faster in moist than in dry air, and faster when the salt is moist than when dry. According to M. Berthelot and G. André, the dry salt has too small a vap. press. for measurement in air, ammonia, or carbon dioxide under a press. of two-thirds of an atm.; the presence of water vapour also has little influence on the vap. press. of the salt, but in the presence of liquid water, the vap. press. is much greater. The vap. press. of the dry salt after many days at 18° was less than 1 mm., but in the presence of a drop of water, the vap press. was 8·4 mm. and, after 10 hrs., 61 mm. when it remained constant; with more water, the vap. press. attained 67·8 mm., and. after 24 hrs., 122·3 mm. without reaching a constant value, for, after 3 days, it reached 135 mm. When two vessels, one containing water and the other a conc. soln. of ammonium carbonate, are confined in an atm. of carbon dioxide under a bell-jar, for about eight days, the distribution of ammonia and carbon dioxide is uniform in both vessels.

Like the normal carbonate, when the hydrocarbonate is heated in a retort, a little of it is decomposed into carbon dioxide, water, and ammonia: $NH_4HCO_3=H_2O+NH_3+CO_2$, and at 49° it yields a few drops of liquid distillate which crystallizes in needles, and the remainder undergoes no further change. These three substances reform the hydrocarbonate and the salt remains dry. At a higher temp., the salt remaining in the retort becomes wet, and a moist solid no longer having the composition of the hydrocarbonate condenses in the neck of the retort, and carbon dioxide escapes. While the hydrocarbonate furnishes the same salt when the distillation is conducted slowly enough, if the salt be distilled faster than the whole of the products of distillation can condense in the receiver, commercial ammonium carbonate, $(CO_2)_2H_2O(NH_3)_3$, is formed: $3(NH_4)HCO_3=(CO_2)_2H_2O(NH_3)_2+2H_2O+CO_2+NH_3$.

According to C. L. Berthollet, 100 grms. of water at 15° dissolve 12·5 grms. of hydrocarbonate. H. C. Dibbits found the number of grams of ammonium hydrocarbonate in 100 grms. of sat. soln. of different temp., to be:

	0°	5°	10°	15°	20°	25°	30°
Grms. of salt . .	10·6	12·1	13·7	15·5	17·4	19·3	21·3

P. P. Fedotieff has studied the effect of ammonium chloride, sodium hydrocarbonate, and of sodium chloride on soln. of ammonium hydrocarbonate in connection

with the ammonia process for sodium carbonate—*q.v.* When the aq. soln. of the hydrocarbonate is exposed to air, it rapidly loses carbon dioxide, but, as indicated by C. L. Berthollet, this loss is soon arrested. J. Davy observed that if the soln. be placed in contact with the solid, even at low temp., the latter is decomposed with the evolution of bubbles of carbon dioxide. J. Dalton concluded that a sat. soln. of the hydrocarbonate dissolves carbon dioxide to the same extent as water, and hence concluded that under these conditions no ammonium carbonate could be formed containing more carbon dioxide than the hydrocarbonate. According to J. Davy, however, a sat. soln. of the hydrocarbonate is a sat. soln. of carbon dioxide, and hence he doubted if the hydrocarbonate really exists in soln., although a sat. soln. deposits crystals of the hydrocarbonate when cooled. C. L. Berthollet found that when a soln. of the hydrocarbonate is heated in a retort it effervesces owing to the evolution of carbon dioxide; a soln. of the normal carbonate first collects as distillate, and finally pure water. The hydrocarbonate is but very slightly affected by cold or boiling conc. aq. alcohol. After the action, the alcohol contains a little ammonia, and a few bubbles of carbon dioxide are probably given off. The boiling alcohol slowly decomposes the hydrocarbonate into carbon dioxide, water, and ammonia. Dry crystals of the hydrocarbonate are not affected by ammonia gas either at 0° or at ordinary temp. According to E. Divers, when the powdered salt and a conc. soln. of ammonia are mixed together there is a hissing noise, the mixture becomes warm, but very little salt dissolves; it is possible that ammonium carbamate, $(NH_3)_2CO_2$, along with some normal carbonate is formed: $2NH_4HCO_3+2NH_3=(NH_4)_2CO_3.H_2O+CO_2(NH_3)_2$. When the hydrocarbonate is digested with the conc. aqua ammonia in a closed vessel at 20°–25°, considerable quantities of the carbamate are slowly formed: $(NH_4)HCO_3+NH_3=H_2O+CO_2(NH_3)_2$. Probably in the first stage of the reaction, normal carbonate and carbamate are formed, and the former then changes to water and carbamate.

H. Rose said that when an aq. soln. of commercial ammonium carbonate is evaporated over sulphuric acid under reduced press., small crystals are obtained which must be immediately withdrawn from the influence of the sulphuric acid, otherwise they effloresce and pass into the hydrocarbonate. If the ebullition of the soln. be not prevented during the evaporation, crystals of the hydrocarbonate are also obtained. H. Rose also obtained the ordinary hydrocarbonate by using calcium chloride in place of sulphuric acid. If the ordinary commercial carbonate be evaporated over sulphuric acid, but not under reduced press., the whole decomposes and nothing remains. The salt is very unstable and success in the preparation of the salt depends on a careful adjustment of the conc. of the soln., and the speed of evaporation. Analyses agree with the formula $(NH_3)_8(H_2O)_9(CO_2)_9$, or $(NH_3)_8(H_2O)_8(CO_2)_9.H_2O$; but although E. Divers failed to make the salt, he thinks H. Rose was successful, and prefers $(NH_3)_4(H_2O)_9(CO_2)_5$, *i.e.* $4(NH_4)HCO_3.CO_2.5H_2O$, on the assumption that the salt which H. Rose analysed was contaminated with hydrocarbonate, and in order to fit H. Rose's hypercarbonate with a series of ammonium carbonates which he supposes can be obtained by crystallization from aq. soln.—normal, sesqui-, hydro-, and perhydro-carbonate.

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§ 34. Carbamic Acid and the Carbamates

In J. L. Gay Lussac's [1] researches on the proportion by volume in which ammonia combines with carbon dioxide, it was found that the dry gases unite in the proportions by volume $NH_3 : CO_2 = 2 : 1$, forming a white solid which condenses partly as flocculi, and partly as an incrustation on the walls of the vessel in which it is formed. Heat is evolved during the reaction. J. Davy says that the gases combine in the same ratio whatever be their proportions in the mixture. In preparing the solid by this process, a mixture of carbon dioxide with twice its volume of ammonia is passed through a number of glass tubes cooled to a very low temp. The solid collects as a sublimate in the tubes which are afterwards cut to pieces, to recover the solid. R. E. Hughes and F. Soddy found that if the two gases be very thoroughly dried, not the faintest sign of the formation of ammonium carbamate occurs after the gases have stood in contact for 24 hrs. K. Buch found that by mixing dry liquid ammonia and solid carbon dioxide in vacuo, the product has never the exact stöchiometrical composition, for there is always a small excess of either absorbed ammonia or carbon dioxide. F. E. C. Scheffer found that a tube containing ammonia with a great excess of carbon dioxide showed a rapid vanishing of the meniscus at 31° in presence of the solid carbamate, and on the carbon dioxide side there was a critical end point, and on the ammonia side, a separation at about 120°.

The product was formerly regarded as the anhydrous normal ammonium carbonate, but with the development of J. J. Berzelius' ammonium theory, it was recognized that the product of this reaction is an altogether different compound and to it the name **ammonium carbamate** was applied. It was found that this compound is a salt of the monamide of metacarbonic acid, to which the name **carbamic acid,** $NH_2.CO.OH$, was applied. The monobasic acid has not been isolated in the free state, but both ethereal and inorganic salts are known—*e.g.* urethane or ethyl carbamate, $NH_2.CO.OC_2H_5$; carbamic chloride, $NH_2.CO.Cl$; etc. Ammonium carbamate, $NH_2.CO.ONH_4$, is related to metacarbonic and carbamic acids as illustrated graphically in the following scheme:

$$\begin{matrix}HO\\HO\end{matrix}{>}C{=}O \qquad \begin{matrix}HO\\NH_2\end{matrix}{>}C{=}O \qquad \begin{matrix}NH_4O\\NH_2\end{matrix}{>}C{=}O$$

Metacarbonic acid. Carbamic acid. Ammonium carbamate.

The reactions involved in the preparation of ammonium carbamate are essentially either the union of carbon dioxide and ammonia, or the dehydration of ammonium carbonate. A. Basaroff prepared ammonium carbamate by passing the mixture of dried ammonia and carbon dioxide gases into well-cooled absolute alcohol. A copious crystalline precipitate is formed. This is separated by filtration from the mass of liquid, and heated with absolute alcohol in a hermetically sealed vessel to 100°–110° when the liquid on cooling deposits the salt in laminæ. These are pressed between filter paper, and dried over potassium hydroxide. A. Mente says the process furnishes a highly pure product, but the cost is high. When the crystals are powdered, they attract moisture from the air, and if the mass is then dried over sulphuric acid or potassium hydroxide, the composition of the product is not quite the same as before.

E. Divers made the salt (1) by passing a mixture of the two gases into conc. aqua ammonia, when the carbamate separates in crystals. The details resemble those employed in A. Basaroff's process, except that conc. aqua ammonia is used in place of alcohol. E. Divers also prepared the salt (2) by digesting in a closed vessel aq. ammonia sat. at a low temp. with any of the ammonium carbonates at 20°–25° for 36–48 hrs., when the carbamate either crystallizes out at once, or will do so after adding more carbonate, repeating the digestion, and again cooling. The commercial carbonate gives the best yield. E. Divers obtained the carbamate (3) by heating commercial carbonate mixed with a sufficient quantity

of anhydrous potassium carbonate in a retort immersed in a water-bath at a temp. carried slowly from 50° to 80°, and connecting the neck of the retort with a wide tube dipping under mercury. The neck of the retort soon becomes incrusted with a translucent crystalline mass of the carbamate. There is a slightly less yield if finely powdered anhydrous calcium chloride be substituted for potassium carbonate when much carbon dioxide escapes at about 48°, and the incrustation begins to form at about 52°, and continues to do so as the temp. rises slowly to 65° when the process will be completed. From $1\frac{1}{2}$ to 3 times as much calcium chloride as carbonate is used, and a layer of the powdered chloride should be spread over the mixture. The carbamate can be purified by redistillation from fresh calcium chloride. The carbamate can indeed be obtained by distilling the commercial carbonate very slowly, at a heat not exceeding 60°, the more remote part of the incrustation is impure carbamate. E. Divers found that (4) by distilling commercial carbonate with aq., or perhaps better, absolute alcohol, ammonium carbamate is formed; and he obtained (5) a soln. of the carbamate by repeatedly dissolving the commercial carbonate in the same quantity of water and cooling after each addition so as to remove the normal ammonium carbonate. The soln. is then nearly sat. with ammonia gas, and when the ammonium carbonate has been removed a soln. of the carbamate contaminated with a little carbonate is formed. H. Rose, and E. Divers made ammonium carbamate by distilling ammonium chloride or sulphate with dry potassium, sodium, or calcium chloride. H. Rose prepared ammonium carbamate by sublimation from an intimate mixture of ammonium amido-sulphite, $NH_2.SO_3.NH_4$, and anhydrous sodium carbonate in such a way that no moisture had access to the vessel. The salt is obtained as an incrustation on the walls of the condensing vessel. The reaction here involves the formation of ammonia and carbon dioxide: $NH_2.SO_3.NH_4+Na_2CO_3=Na_2SO_4+2NH_3+CO_2$, a reaction which can be compared with that between the amido-sulphate and sodium hydroxide: $NH_2.SO_3NH_4+NaOH=NaHSO_4+2NH_3$. The mixed gases on cooling form the carbamate. T. Peters obtained this compound by heating ethyl aceto-acetate with water-free alcoholic ammonia to 180° in a tube, or by the action of ammonia gas.

Ammonium carbamate forms transparent crystalline plates belonging possibly to the rhombic system; it also occurs in amorphous white flocculi, and in crystalline masses. Analyses of the dried product by H. Rose, E. Divers, and A. Basaroff correspond closely with the requirements for $CO_2(NH_3)_2$. The carbamate has a strong ammoniacal smell not equal to that of normal ammonium carbonate or sesquicarbonate. The taste also is less caustic than that of normal ammonium carbonate. When freely exposed to air, ammonium carbamate gradually deliquesces, and by a prolonged exposure, it is nearly all dissipated; the residue is a kind of skeleton of the original fragment, and it is the hydrocarbonate: $NH_4O.CO.NH_2+H_2O=(NH_4)HCO_3+NH_3$. The deliquescence of the carbamate, said E. Divers, "is an interesting fact not only as affording evidence that the carbamate has only a slowly manifested affinity for water, but also as distinguishing between the mere physical attraction of a body for water and its chemical transformation with water into a new substance." F. W. Raabe's value for the heat of formation or dissociation between 7° and 11°, and 765 mm. press. is $(CO_2,2NH_3)$ 39·3 Cals.; E. Lecher gives 37·7 Cals. per mol. of carbon dioxide with two of ammonia, at 17° and 710 mm.

Unlike the carbonates, ammonium carbamate does not fuse when heated, but, as was observed by J. Davy, it is converted into a gas at 60°. F. E. C. Scheffer was unable to establish a definite relation between the press. and the sublimation temp. for ammonium carbamate since the results were very irregular and dependent upon a variety of circumstances—rate of rise of temp., etc. The hypothesis suggested by W. D. Bancroft, and by C. van Rossem is that the observed results are produced by the superposition of two phenomena dependent on: (i) the speed of vaporization, and (ii) the speed of dissociation. J. H. van't Hoff half filled a

thick-walled glass tube about 10 cm. long with the salt, and after removing the air, sealed up the tube. The tube was then heated; the salt melted at about 140°, and the vapour continuously increased at the cost of liquid. The tube burst before the liquid had all passed to the vapour phase. He therefore failed to observe a "critical point" analogous to the physical phenomenon of evaporation; but he did obtain a successful result with a mixture of hydrogen phosphide and chloride. According to E. Briner, the m.p. under press. 152° is a triple point. According to A. Basaroff, when heated in a sealed tube between 120° and 140°, ammonium carbamate passes into urea: $NH_4O.CO.NH_2 = CO(NH_2)_2 + H_2O$. When ammonium carbamate is converted into gas or vapour at any temp., it appears to be decomposed into its components carbon dioxide and ammonia. The odour of ammonia which it emits at ordinary temp. is evidence of this unless it be assumed that the compound smells exactly like ammonia. The vapour density calculated from the mixture of two volumes of ammonia with one of carbon dioxide is 0·8993, and for $NH_4.CO_2.NH_2$, 1·349; A. Bineau found 0·90; H. Rose, 0·8992; and A. Naumann, between 37° and 100°, 0·892. A. Bineau also showed that the same result is obtained at ordinary temp. as at distilling temp. A. Bineau also noticed that the gaseous product obtained by heating the salt remains gaseous at a temp. lower than that at which it is formed. A. Naumann's values for the vap. press., p, of the salt soln. at different temp.:

	−15°	−10°	0°	10°	20°	30°	40°	50°	60°
p, mm.	2·6	4·8	12·4	29·8	62·4	124	248	470	770

The curve for the dissociation press. rises steadily with a rise of temp. and corresponds exactly with the vap. press. curves of liquids and solids. These results agree with the values obtained by G. Erckmann, and F. Isambert; the latter also measured the effect of an excess of each of the products of dissociation—ammonia and of carbon dioxide. R. Engel and A. Moitessier claim to have established the relation that when two gaseous bodies on combining give a dissociable compound, the combination takes place only when the sum of the press. of the components is greater than the press. of dissociation of the compound, whatever may be the press. possessed by each of the bodies. Accordingly, if a dissociable body is placed in the presence of one of the substances produced by its dissociation, at a press. equal to or greater than the press. of dissociation at the temp. of the experiment, or if a mixture in any proportion of the components is present (provided the sum of their press. is equal to the press. of dissociation), the dissociation of the body cannot take place. This rule, says F. Isambert, can be more neatly expressed: If the press. of a gas is less than the maximum press. in a vacuum, the total press. will be at this maximum, and, conversely, the value will remain the same as that of the free gas; and F. Isambert adds that the rule is not true. In the case of ammonium carbamate, the total press. in the presence of an excess of one of the component gases is always greater than the maximum press. in vacuo; and therefore a compound may dissociate in presence of one of its products of dissociation at a press. equal to or greater than the dissociation press. C. Matignon and M. Fréjacques represented A. Naumann's dissociation press. between −15° and 60° by $\log p = -3·635T^{-1} - 7·045 \log T + 28·692$; and $\log p = -4·821T^{-1} - 15·4 \log T + 53·3586$; and hence he calculated the heat of dissociation of ammonium carbonate, at constant press., to be −39 cals.

A. Naumann observed that the velocity of the dissociation of the solid and the recombination of the vapour is increased by increasing the surface area of the solid; these velocities are proportionally smaller the nearer the observed press. is to the equilibrium value; and the velocity of dissociation is greater the higher the temp. A. Horstmann has shown that the law of mass action describes the relation between the partial press. of ammonia and carbon dioxide, and that the dissociation press. is not perceptibly influenced by the presence of an indifferent gas—e.g. air—while the dissociation press. in the presence of one of the products of dissociation is smaller than in vacuo. In general, the total press. of the gases uniting to form a

solid and in equilibrium with that solid is least when the gases are in the same proportion as they exist in the solid phase.

From the equation $NH_4O.CO.NH_2 \rightleftharpoons 2NH_3+CO_2$, and the mass law, and remembering that the carbamate is a solid, $C_1C_2^2$=constant, when C_1 and C_2 respectively denote the conc. of the carbon dioxide and ammonia, and the solid phase is present. By Boyle's law, the press. of a gas is proportional to its mass conc., so that if p_1 denotes the partial press. of the carbon dioxide, and p_2 that of the ammonia, $p_1p_2^2=K$, where K is the dissociation constant. E. Briner found the value of K at 77·2° to be nearly 1·5; and at 98·5°, K=39·5, with these data the heat of dissociation (assumed independent of temp.) can be readily calculated from the well-known expression $(d \log K)/dT=-q/RT^2$. If P be the total press., $P=p_1+p_2$; and consequently, by substitution for p_1, it follows that $P=Kp_2^{-2}+p_2$, an expression which has a minimum value when $p_2^3=2K$, *i.e.* when $p_2=2p_1$. Consequently, if either of the products of dissociation be in excess of these proportions, the total press. will be increased in vacuo.

According to E. Divers, 100 parts of water dissolve about 66·7 grms. of the salt, and the temp. is depressed during the process of soln. It dissolves without change as ammonium carbamate, but soon combines with water and a definite state of equilibrium is established between the carbamate and carbonate: $NH_4O.CO.NH_2+H_2O \rightleftharpoons (NH_4)_2CO_3$, as indicated by the work of H. J. H. Fenton, F. E. C. Scheffer, K. Buch, B. Becker, A. C. Cumming, J. Natanson, L. Bourgeois, F. Fichter, and J. J. R. McLeod and H. D. Haskins in connection with the right member of this equation—*q.v.* The degree of hydration of the carbamate was found by K. Buch to increase with the dilution:

Carbamate : Water	1 : 200	1 : 300	1 : 400	1 : 500
Degree of hydration	0·749	0·796	0·845	0·966

K. Buch measured the partial press. of ammonia and carbon dioxide in mixtures of ammonium carbonate and carbamate, and from the results calculated the conc. of the free and bound ammonia and higher carbonate, and of the carbamate and carbonic acid. The hydrolysis and equilibrium constants were then calculated. The hydrolysis constants K_1 and K_2; and the equilibrium constant K_3 of the hydrocarbonate to carbamate, were:

$$K_1=\frac{p_{NH_3}p_{CO_2}}{[NH_4^{\cdot}][HCO_3']};\quad K_2=\frac{p_{NH_3}p_{CO_2}}{[NH_4^{\cdot}][NH_2COO']};\quad K_3=\frac{NH_3HCO_3'}{[NH_2COO']}$$

where K_1=37 to 69; $K_2=39-84\times10^8$; and K_3=0·42 to 1·68. It was assumed that ionization was complete, but this is not strictly valid for the conc. soln. employed.

J. Davy found ammonium carbamate to be soluble in alcohol of sp. gr. 0·829; and A. Basaroff found that it dissolves when heated with absolute alcohol in a sealed tube, and it crystallizes out again when the soln. cools. E. Divers also found that ammonium carbamate dissolves freely in aqua ammonia, and the system is cooled; 100 parts of aqua ammonia dissolve 50 parts of the salt, and the soln. on standing furnishes crystals of normal ammonium carbonate; but if the freshly prepared soln. be cooled to 0°, crystals of the carbamate are obtained, consequently ammonia retards the hydrolysis of the carbamate.

According to H. Rose, dry chlorine attacks ammonium carbamate very slowly without the liberation of water; ammonium carbamate is not perceptibly affected by dry hydrogen chloride in the cold; but if warmed, it is decomposed by the gas without the liberation of water, forming ammonium chloride and carbon dioxide. Aq. acids liberate carbon dioxide, alkali-lye gives ammonia when heated with hydrogen sulphide, no water is produced, but ammonium sulphide, $(NH_4)_2S$, is formed with sulphur dioxide; in the cold, it is coloured pale yellow, and, when heated, an orange-yellow sublimate of $(NH_4)S_2O_4(NH_2)$; according to A. Mente, the vapour of sulphur trioxide furnishes without effervescence, carbon dioxide,

and ammonium sulphate; chlorosulphonic acid, HSO_3Cl, sulphuryl chloride, SO_2Cl_2, or pyrosulphuryl chloride, $S_2O_5Cl_2$, furnishes ammonium imidosulphonate; and it reacts with phosphoryl chloride, $POCl_3$, at 100°, forming di-imido phosphoric acid. According to H. J. H. Fenton, with sodium, it furnishes cyanamide: $NH_4O.CO.NH_2+2Na=2NaOH+CyNH_2+H_2$, as in the analogous case with urea, and with normal ammonium carbonate. H. J. H. Fenton also found that it is rapidly attacked by hypochlorites or hypobromites. With hypochlorites, only half the total nitrogen is evolved as a gas. Similar results were obtained with chlorites and bromites. If sulphur dioxide be added to the soln. treated with *sodium hypochlorite, ammonia is formed. If boiled with an excess of ammonia* and calcium chloride, calcium carbonate is formed. A. Mente noted that with acid chlorides, if the temp. be kept below the dissociation of the carbamate, the NH_4-radicle unites with chlorine to form ammonium chloride; the NH_2-radicle takes the place of the chlorine atom in the acid chloride and carbon dioxide is evolved; for example: $CH_3CO.Cl+NH_4O.CO.NH_2=NH_4Cl+CH_3.CO.NH_2+CO_2$. The carbamate sometimes acts like ammonia gas and an imide is formed. H. Kolbe found that when heated with zinc ethyl, $Zn(C_2H_5)_2$, ammonium carbamate gives no sign of *propionic* acid or *propion-amide*. E. Divers adds that a mixture of the carbamate with anhydrous calcium chloride can be distilled without any sign of chemical change.

If ammonium carbamate be treated with less than its eq. of calcium chloride, it soon gives a precipitate, and the filtered soln. gives no further precipitation when heated. *The reaction is the same as when calcium chloride is added in excess.* An ammoniacal soln. of calcium chloride gives an instantaneous but slight precipitate when treated with an excess of a soln. of ammonium carbamate. The precipitate increases slowly on standing, and next day, when boiled, the supernatant liquor gives a copious precipitate. The immediate precipitation is presumably due to the presence of ammonium carbonate, and the subsequent precipitation is due to the slow conversion of carbonate to carbamate in the presence of free ammonia. Hence, an ammoniacal soln. of calcium chloride gives an immediate precipitation with an *excess of ammonium carbonate* and a very slow *precipitation* with an excess of the carbamate.

A very conc. ammoniacal soln. of ammonium carbamate with a sat. soln. of calcium chloride gives a precipitate which is soluble in water and which has a composition indicating that it is either $(CO_2NH_2)_2Ca$, calcium carbamate, or calcium ammoniocarbonate, $(NH_4)_2CO_3.CaCO_3$. E. Divers *inclines to the belief* that the precipitate is really **calcium carbamate**—presumably $Ca(O.CO.NH_2)_2$—possibly $HO.CaO.CO.NH_2$. E. Drechsel prepared calcium carbamate as a fine white powder consisting of small flat prisms by crystallization from a sat. soln. in warm aq. ammonia: $(NH_2CO_2)_2Ca.\frac{1}{2}H_2O$. The aq. soln. is unstable, and it is decomposed by its own water of crystallization, so that when freshly prepared it has no smell, but it soon acquires an ammoniacal smell. At 95°–100°, it is partially decomposed into a mixture of carbonate and carbamate: $2\{(NH_2.CO_2)_2Ca.\frac{1}{2}H_2O\}=NH.CO.NH_4+CaCO_3+(NH_2CO_2)_2Ca$; and at the *softening point of glass*: $(NH_2.CO_2)_2Ca=CaCN_2+2H_2O+CO_2$; some cyanide is also formed. Minute shining plates of **strontium carbamate,** $(NH_2.CO_2)_2Sr$, were also made by E. Drechsel and found to be *more* stable than the calcium salt. E. Divers obtained a precipitate—**barium carbamate**—by mixing a barium salt, and a soln. of ammonium carbamate. E. Drechsel only succeeded in making **barium chloro-carbamate,** $BaCl_2.Ba(NH_2.CO_2)_2$; nor did he succeed in making **lithium carbamate,** but fine prisms of hydrated **sodium carbamate,** $NaO.CO.NH_2$, were obtained which effloresce in air, and become anhydrous over sulphuric acid. When the *anhydrous* salt is heated, it decomposes: $NH_2CO.ONa=H_2O+NaN:CO$; and the hydrated salt: $2(NH_2.CO.ONa)+nH_2O=(n-1)H_2O+Na_2CO_3+NH_2.CO.ONH_4$. Small deliquescent needles, and prisms of **potassium carbamate,** were obtained in several ways. It decomposes like the sodium salt. In no case was cyanamide

obtained in the decomposition of the alkali carbonates, but with those of the alkaline earths, cyanates are first formed; and urea is assumed to be derived from ammonium carbonate mediately through the cyanates. E. Divers' precipitates are not to be confused with those previously described. The precipitate with ammonium carbamate and an alkaline earth chloride is more soluble than the precipitate with the carbonate.

R. Ehrenfeld found that the carbamate in commercial ammonium chloride is not reduced by hydrogen at the cathode during electrolysis. If the current be rapidly reversed during the electrolysis of soln. of commercial carbonate (containing carbamate), with platinum electrodes, E. Drechsel found after 8 hrs. a salt of a platinum base is contained in the soln. There is also formed in the first or oxidation state: $NH_4O.CO.NH_2+O=H_2O+CO_2(NH_2)_2$; and this undergoes a further transformation into urea: $CO_2(NH_2)_2+H_2=CO(NH_2)_2+H_2O$. B. Gerdes also obtained platinum bases in the electrolysis of soln. of ammonium carbamate in a cell with platinum electrodes.

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§ 35. Commercial "Ammonium Carbonate"

This product is also called *sal alkali volatile, sal volatile salis ammoniaci*; and, as previously indicated, owing to its formation during the dry distillation of bones, horns, and other animal products, *spirit of hartshorn, sal volatile cornu cervi*, etc. It is the *ammonii carbonas* of the pharmacopœia.

According to E. Divers,[1] the product obtained by cooling a mixture of three volumes of ammonia with two volumes of carbon dioxide in the presence of at least the calculated quantity of water vapour furnishes a substance similar to the ordinary commercial carbonate; a greater proportion of carbon dioxide can be used if sufficient water vapour and some liquid water are present. E. Divers also found the same compound to be formed by the rapid distillation of any of the ammonium carbonates or of ammonium carbamate with water.

Ammonium carbonate is prepared on a large scale by distilling an intimate mixture of ammonium sulphate with twice its weight of chalk in cylindrical cast-iron vessels, 7 to 10 ft. long and 1½ ft. diameter, and fitted with movable leaden covers at each end. Several retorts are heated in one furnace. The vapours from the retorts are led into stone chambers where the carbonate is deposited as a crust

on the walls. When the crust is sufficiently thick, it is detached by knocking the walls. The crude carbonate is mixed with 43–44 per cent. of chalk, and resublimed in pots covered by leaden caps, and heated by a water-bath between 70° and 80°. About 34 per cent. of the mixture employed is recovered as sublimed ammonium carbonate, and 59–60 per cent. of calcium sulphate. A certain proportion of ammonia or ammonium carbonate escapes in each operation, and the exit gases are therefore passed through a small scrubber where they meet a stream of sulphuric acid which retains the uncondensed carbonate, and the free ammonia as ammonium sulphate. G. Lunge recommended passing a stream of carbon dioxide through the chamber in order to get a more complete recovery of the ammonia. H. Kunheim recommended passing ammonia gas obtained by the distillation of gas liquor directly into the condensing chambers where it meets a stream of carbon dioxide, obtained as a by-product from lime kilns or other manufacturing processes, and deposits the carbonate as a crust. Ammonium chloride can be used in place of the sulphate, and this has been the subject of patents by C. Wigg and J. W. Pratt, etc., although the process is a very old one.

Neither ammonium carbonate nor ammonium carbamate can exist as vapour, for both these compounds decompose into their constituents when heated. The nature of the products obtained by the distillation of ammonium chloride with calcium, potassium, or sodium carbonate, depends on the behaviour of a mixture of water vapour, ammonia, and carbon dioxide; or, since these substances do not combine until their temp. is below the condensing point of steam, and therefore much of the water separates from the mixture in the liquid state, the nature of the products depends upon the reaction of eq. quantities of moist carbon dioxide and moist ammonia, and the behaviour of the product of this reaction with liquid water. It is therefore assumed that the products of the distillation are ammonia, water, and the salt $2(NH_4)HCO_3.CO.NH_2$. E. Divers believes that this is not a satisfactory explanation of the reaction since he found that the first product of the distillation of a mixture of calcium carbonate and ammonium chloride is ammonium carbamate notwithstanding the presence of water, "and that a substance with the composition of the commercial carbonate is formed when the moist carbamate is redistilled." O. Figuier obtained no calcium oxychloride, if formed, but E. Divers usually found some oxychloride; O. Figuier also obtained no ammonia, but he cooled his receiver with ice and assumed any ammonia which might be formed was arrested by the condensed liquid. E. Divers obtained no ammonia in the early stages of the distillation. If alkali carbonates be substituted for calcium carbonate, ammonia is given off from the very first, owing to the fixation of water and carbon dioxide from the dissociated ammonium carbonate by the cool alkali carbonate: $K_2CO_3+CO_2+H_2O+2NH_3=2KHCO_3+2NH_3$. At a later stage, this absorbed carbon dioxide is again set free to combine in part with some of the deposited "carbonate of ammonia." During the redistillation of the primary product, E. Divers found that an evolution of ammonia gas commences between 50° and 55°.

C. Raspe treated the ammoniacal liquid derived from the distillation of coal, bones, etc., with zinc carbonate to remove the sulphur, and finally distilled the product—the empyreumatic matters were removed by passing the vapours through hot coke. An acid carbonate is also made on a large scale from aqua ammonia (from gas liquor) and carbon dioxide. The product has 21–23 per cent. of ammonia. It decomposes more slowly than the ordinary commercial carbonate containing 31 per cent. of ammonia. According to P. Seidler, it furnishes the commercial carbonate when resublimed, as in the 1846 patent of F. C. Hills.

There have been several patents for treating the ammonium chloride liquors filtered from the hydrocarbonate obtained in preparing sodium carbonate by E. Solvay's process. For example, J. Young decomposed the soln. of ammonium chloride by boiling it with calcium of magnesium carbonate; F. L. Teed passed the liquid down a tower packed with lumps of limestone, but neither process was

very successful. H. Schreib made a special study of the action of a soln. of ammonium chloride on calcium carbonate—it proceeds three times as fast with powdered marble, and twice as fast with powdered limestone as it does with freshly precipitated calcium carbonate. The action is slower with limestone in lumps than in powder. The reaction is rapid at first, but afterwards proceeds slowly, taking a long time for completion.

The impurities in commercial carbonate may include ammonium thiosulphate derived from the ammonium sulphate or ammonium chloride containing some sulphate; ammonium sulphate or chloride, derived from the same sources; lead, derived from leaden receivers; and lime, calcium chloride, or other non-volatile substances may be present, and these remain as a permanent residue where the salt is volatilized.

The commercial carbonate has a conchoidal fracture, or it may occur in softer cakes of prisms arranged perpendicularly to the surface of deposition, or it may occur in white nearly opaque layers. When subjected to a high press. of 50–100 atm., W. Hempel obtained the commercial carbonate in masses of stone-like hardness. The chemical composition of the different samples is, however, fairly constant, which approximates to CO_2, 55·93; NH_3, 28·81; H_2O, 15·26 per cent. corresponding with $(CO_2)_3(H_2O)_2(NH_3)_4$. T. O. Bergman's old analysis, made in 1774, gave CO_2, 45, NH_3, 43; J. Dalton's, made in 1813, CO_2, 59; NH_3, 24·5; and analyses between 1817 and 1853, made by A. Ure, R. Phillips, T. Thomson, J. Davy, and H. Rose, ranged from 50·55 to 56·23 per cent. CO_2, and 26·17 to 30·5 per cent. NH_3. J. Dalton deduced from his analysis the atomic composition generally adopted in chemistry up to 1870, and which he represented as eq. to one mol. of "subcarbonate," *i.e.* hydrocarbonate, and two of the "carbonate," *i.e.* the carbamate. E. Divers showed that there had been a change in the manufacturing process which furnished a product with 31 per cent. of NH_3 and 56 per cent. of CO_2 corresponding with $(CO_2)_2(H_2O)(NH_3)_3$, differing in many of its properties as well as in composition from the older commercial carbonate. The constitution of the commercial carbonate is $(NH_4)HCO_3.NH_4O.CO.NH_2$, corresponding with that required by a double salt of ammonium hydrocarbonate and carbamate, or else a mixture of these two salts. E. Divers favoured the former hypothesis. The older commercial carbonate corresponded with $2(NH_4)HCO_3.NH_4O.CO.NH_2$, and can therefore be regarded as having been a mixture of the new carbonate with some hydrocarbonate. Some differences are:

In 1839, H. Rose said that the ordinary commercial carbonate liquefied when slowly heated in a retort; whereas, in 1870, E. Divers found scarcely any liquefaction. The older carbonate when distilled with anhydrous calcium chloride gave ammonium chloride, calcium carbonate, and carbon dioxide, whereas the newer carbonate gave in addition ammonium carbamate. The solubility of the newer carbonate is about twice as great as the old; and the aq. soln. is not charged with carbon dioxide. R. Phillips and E. Divers have also reported as rare the occurrence of the hydrocarbonate in commercial carbonate. In consequence of these differences it is necessary to know whether the old or the new carbonate is in question when discussing the properties of the commercial carbonate. Sometimes the sesquicarbonate is to be understood.

E. J. Maumené (1880), K. Kraut (1886), L. L. de Koninck (1894), E. O. von Lippmann (1888), etc., have given analyses of commercial samples. According to J. Dalton (1819), when the older commercial carbonate is exposed to air, it loses about 50 per cent. in weight, while, according to E. Divers (1870), the more recent carbonate loses 43–44 per cent. In either case, the white residue was observed by J. Dalton, E. Divers, and H. Vogler to consist of ammonium hydrocarbonate, $(NH_4)HCO_3$. The commercial carbonate gets moist when heated. When slowly distilled, the product has virtually the same composition as before, except that at the beginning a little normal carbonate is formed, and towards the end, some hydrocarbonate appears. A. Basaroff found that when heated in sealed tubes to 130° it is converted into urea, $CO(NH_2)_2$.

The ordinary method of determining the solubilities cannot be applied to the commercial carbonate because a sat. soln. decomposes any fresh carbonate added to it. F. Rüdorff found the temp. fell from 15·3° to 3·2° when 25 parts of salt are dissolved in 100 parts of water. E. Divers found that 100 parts of water at 15° dissolve 25 parts of the commercial salt, and at about 65°, 66·7 parts. When the sat. soln. is cooled, it furnishes crystals of the hydrocarbonate. T. J. Pelouze and E. Frémy [2] said that the sesquicarbonate separates under these conditions, but in E. Divers' opinion this statement is wrong. According to J. J. Berzelius, 100 parts of water at 49° dissolved 50 grms. of the old carbonate of commerce. In a general way, E. Divers has shown that the solubility of the commercial carbonate approximately accords with the hydrocarbonate it contains—viz. one of the salt in two of water. G. Lunge measured the sp. gr., D, of soln. of ammonium sesquicarbonate and found this constant rose from 1·005 with 1·66 per cent. of salt to 1·144 with 44·90 per cent. of salt, at a temp. 12°. Some intermediate values are :

Per cent. salt	3·18	6·04	11·86	17·70	23·78	29·93	36·88	44·29
Sp. gr.	1·010	1·020	1·040	1·060	1·080	1·100	1·120	1·140

T. Griffiths found a cold sat. soln. of the old carbonate to boil at 82° ; J. Davy says such a soln. decomposes with the formation of bubbles of gas at a lower temp. than this. Probably the two observers attached a different meaning to the term "boiling." At 100°, T. Griffiths found the soln. to have given off all the carbonate it contained and to be nothing but water. E. Divers found a sat. soln. of the new carbonate begins to effervesce at 60°, and does so copiously at 75°—the first products of the effervescence are carbon dioxide, but at 85° ammonia is also present, and a liquid condenses on the neck of the retort. E. Divers says the first action of water is to split the salt into the acid carbonate crystals and ammonium carbamate which remains in soln. : $(NH_3)_3H_2O(CO_2)_2=(NH_4)HCO_3+CO_2(NH_3)_2$; the carbamate in soln. is hydrolyzed to the normal carbonate, $CO_2(NH_3)_2+H_2O=(NH_4)_2CO_3$, which then reacts with the commercial carbonate forming crystals of the sesquicarbonate, and a soln. of the carbamate, $2(CO_2)_2H_2O(NH_3)_3+(NH_4)_2CO_3+H_2O =(NH_4)_4H_2(CO_3)_3.H_2O+2CO_2(NH_3)_2$. The carbamate so formed is hydrolyzed, as before, to the normal carbonate which may separate in the crystalline condition, to form the sesquicarbonate and orthocarbonate ; $3(NH_4)_2CO_3.H_2O =(NH_4)_4H_2(CO_3)_3.H_2O+2NH_3+2H_2O$; or $4(NH_4)_2CO_3.H_2O=(NH_4)_4H_2(CO_3)_3.H_2O +(NH_4)_4CO_4+2H_2O$. The carbamate may also form orthocarbamate, $(NH_4O)_2C(NH_2)$, and sesquicarbonate, $4(NH_4O.CO.NH_2)+4H_2O=(NH_4)_4H_2(CO_3)_3 +(NH_4O)_2C(NH_2)_2$. The equations last indicated are hypothetical. The facts are that in the action of water on the commercial carbonate, crystals of hydro-, sesqui-, and normal meta-carbonates can be obtained along with a soln. of ammonium carbamate and what E. Divers assumes to be either ammonium orthocarbonate or orthocarbamate.

Aq. alcohol extracts the carbamate from the commercial carbonate, and leaves a residue of the hydrocarbonate. N. W. Fischer noted that alcohol precipitates the hydrocarbonate from the aq. soln. of the commercial carbonate ; this precipitate was formerly named *offa Helmonti* after J. B. van Helmont, who described it in his essay *De lithiasi* (Amstelodami, 1648). According to L. Hünefeld (1836), when the commercial carbonate is warmed with 90 per cent. alcohol, at 47·5° bubbles of gas begin to rise from the undissolved mass, which increase up to about 60° when there is a copious effervescence of nothing but carbon dioxide. Above 62°, a liquid condenses in the neck of the retort, and this contains the normal carbonate. E. Divers (1870) obtained similar results, but at rather lower temp. than those which L. Hünefeld recorded. The *spiritus ammoniæ aromaticus* of the British Pharmacopœia generally contains an alcoholic soln. of ammonium carbonate with an excess of ammonium hydroxide, with a little oil of lemon and oil of nutmeg. It is made by distilling a mixture of these oils with alcohol, aqua ammonia, and ammonium carbonate.

Conc. aqua ammonia in the cold dissolves carbamate from the commercial carbonate, and it converts the hydrocarbonate into normal carbonate either by removing half its carbonic monohydride, or by combining with it and with water. If the commercial carbonate be digested with a sat. soln. of ammonia in a closed vessel at 20° to 25°, this salt slowly dissolves, and the soln., on cooling, deposits crystals of ammonium carbamate and a little normal carbonate : $(NH_3)_3H_2O(CO_2)_2+NH_3=H_2O+2CO_2(NH_3)_2$. C. Arnold has tabulated the solubilities of the freshly precipitated carbonates and hydroxides of most of the common metals in sat. soln. of potassium and ammonium carbonates. A. Ditte studied the action of soln. of ammonium carbonate on vanadic oxide

G. Gore found that when the commercial carbonate is heated with hydrogen chloride, it swells up, and with liquid hydrogen chloride it gives off no gas, and does not dissolve ; also the product gives no gas with dil. aq. hydrochloric acid. H. Rose observed that when the commercial carbonate is warmed with hydrogen sulphide it is partly converted into ammonium sulphide ; that sulphur dioxide has no action at ordinary temp., but when warmed together, a yellow sublimate of $NH_3.SO_2$ is formed, and then white ammonium sulphite, $(NH_4)_2SO_3$.

When heated to 60° with potassium carbonate, E. Divers found ammonia to be evolved, at 65°, carbamate is formed, and the reaction is completed at 80°, a compound of potassium hydrocarbonate and ammonium carbamate, $(KHCO_3)_2NH_4O.CO.NH_2$, is formed in the first stage of the reaction, say : $(NH_3)_3H_2O(CO_2)_2+K_2CO_3=(KHCO_3)_2CO_2(NH_3)_2+NH_3$. This product is taken to be the potassium analogue of commercial ammonium carbamate, which in the second stage of the reaction decomposes to carbon dioxide and ammonia which condense to ammonium carbamate: $(KHCO_3)_2CO_2(NH_3)_2=2KHCO_3+[CO_2+2NH_3]$, so that the content of the retort at the end is nearly all potassium hydrocarbonate. Again, when heated with dry calcium chloride to 50°–52°, a little carbamate appears and carbon dioxide is evolved. The amount of carbon dioxide evolved gradually diminishes as the temp. approaches 60° : $2(CO_2)_2H_2O(NH_3)_3+2CaCl_2=2CaCO_3+4NH_4Cl+[CO_2+2NH_3]+CO_2$—the bracketed products condense as carbamate —a mixture of unchanged calcium chloride, ammonium chloride, and calcium carbonate remains. When commercial carbonate is mixed with dihydrated calcium chloride, the smell of ammonia disappears, the mixture gets warm, swells up, and evolves carbon dioxide. When eq. proportions are used, and, after the preliminary action has subsided, heated to 50°, nothing but carbon dioxide and water are evolved, and a porous mass of ammonium chloride and calcium carbonate remains. Dry sodium chloride suffers no change, but if moisture be present, some ammonium chloride and sodium carbonate appear to be formed. H. R. Ellis found that when commercial ammonium carbonate is heated with magnesium powder, amorphous carbon and some graphite are formed. J. D. Riedel examined the action of commercial ammonium carbonate on zeolites ; and R. Warrington has studied the nitrification of ammonium carbonate soln.

R. Ehrenfeld observed the formation of ammonium formate during the electrolysis of soln. of commercial ammonium carbonate (with one part of aqua ammonia, sp. gr. 0·910, and four parts water) in a cell with a porous diaphragm, and with zinc or amalgamated zinc cathodes and with a current density of 0·01 to 0·08 amp., and a current of 5 to 10 volts for 12 hrs. at ordinary temp. There is no reduction with cathodes of copper, iron, nickel, lead, or platinum. The amount of reduction depends on the current density and on the conc. of the soln. No formate was detected when the current density was below 0·01 amp., and the conc. below one-fifth that stated above. The formation of the formate is attributed to the presence of NH_4CO_3'-ions in the conc. soln. and not to the presence of carbamate in the commercial carbonate. Analogous experiments with the alkali carbonates gave no formates, although A. Coehn and S. Jahn obtained formates during the electrolysis of aq. sodium hydrocarbonate.

Ammonium carbonate is used in wool-scouring, silk washing, dyeing, and in

the manufacture of baking powders. It is also used medicinally as a gastric stimulant in dyspepsia; as a cardiac and general stimulant in syncope, for stimulating the respiratory movements; as an aid in the expulsion of thick mucus; and also as an emetic.

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§ 36. The Alkali Nitrates

R. Boyle,[1] in 1667, obtained fixed alkali by the calcination of nitre, and he regenerated the nitre by the action of nitric acid on the fixed alkali. J. Mayow accordingly regarded *sal nitrium* as a compound of acid and alkali. L. Lemery (1717), F. Geoffroy (1717), and G. Stahl (1723) took the same view. J. Bohn (1683) first clearly distinguished the crystals of potassium and sodium nitrates, and R. Boyle's description of the crystals shows that he had prepared the sodium salt in 1667. J. G. Wallerius [2] again emphasized the difference between the crystals of sodium and potassium nitrates in 1750, and this was confirmed by J. B. L. Romé de l'Isle in 1783; and by R. J. Haüy in 1822; A. Breithaupt called sodium nitrate *Zootinsalz;* and W. Haidinger, *Nitratin*.

Relatively small amounts of nitrates occur in nature as impregnations or efflorescences on other minerals. They are formed by the decomposition, under special conditions, of the organic matter in soils. On account of the relatively large solubility of the nitrates in water, they can only accumulate in the so-called rainless regions—Chile, California, South-West Africa, Middle Asia, etc. A little ammonium nitrate is derived from the atm., where it is produced by electrical discharges acting on the contained nitrogen and oxygen. In comparatively recent times, too, nitrates have been produced artificially by the action of electrical discharges on air. Nitrates are found in exudations from animals—urine, perspiration, and saliva.[3] L. Lemery (1717) found nitre to be present in the juices of certain plants, and A. Boutin found this to be particularly the case with the *amaranthus blitum*, *amaranthus rubus*, and the *amaranthus atropurpureus;* the dried plants contain respectively 11, 16, and 23 per cent. of nitrate. Saltpetre has been reported to be present in onions during summer, where it is formed through the oxidation of ammonia. The potassium of naturally occurring saltpetre is probably

derived from the weathering of felspathic rocks. The deposits of potassium salts, occurring in isolated pockets in various parts of the mountains of South Africa, are assumed by E. G. Bryant to be derived from the excrement of the rock-rabbits, the nitrogen of which, by a process of nitrification, forms nitrates; the base is derived from the rocks below. The nitre deposits occur in the Griquatown beds of the Transvaal geological system. The largest beds occur at Prieska (north-east Cape Colony); a deposit in the Transvaal furnished the old Boer Republican Government with sufficient nitre for the manufacture of gunpowder. Analyses range from 1·2 to 25·88 per cent. potassium nitrate, small, often insignificant amounts of calcium nitrate; potassium sulphate up to about 10 per cent.; sodium nitrate, 1·1 to 22·47 per cent.; and a small amount of sodium chloride. The potassium salt is recovered by washing. There are natural deposits of potassium nitrate in India; and a deposit is reported from Brazil with 89 per cent. of this salt.

Large quantities of sodium nitrate occur in the Argentine, in California, and principally in the rainless zone on the West Coast of South America—Peru, Bolivia, Chili. The salt occurs in large flat basins—*calicheras*—between the ridges on the Tarapaca plateau and Antofagasti in Chili, and the centre of the trade is at Iquique. The district where the nitre beds occur is rainless and devoid of vegetation. Fig. 75 represents a diagrammatic cross-section through a *nitre basin* which will give a rough idea how soda nitre occurs. According to A. Kroczek,[4] there are roughly five not very sharply defined layers: (i) The first or surface layer, named *chuka*, consists of 2 or 3 inches of grey sand and pebbles mixed with a little sodium sulphate and gypsum. The surface itself is almost devoid of vegetation. (ii) Below the surface is a 1-to-5 ft. layer of similar material cemented together with clay and salt and sodium nitrate. This stuff is called by the natives *costra* (a crust). (iii) Below the *costra* is a layer of *sodium chloride*, etc., *resembling costra* and called *conjelo*. (iv) Below the *conjelo* is a white stratum of massive nitre-bearing rock, 1 to 5 ft. thick, which is called by the natives *caliche*. (v) A layer of clay and loam containing some sea fossils and a little salt; it is called *coba*. The bed-rock consists of shale, or limestone, or other rock which may be there outcropped.

FIG. 75.—Diagrammatic Geological Section of Nitre Bed.

Costra is a kind of low-grade nitre rock or caliche running 5 to 17 per cent. sodium nitrate which does not pay to work; the *caliche* runs 18 to 25 per cent., and in exceptional cases 50 to 60 per cent. sodium nitrate—the average runs 20 to 30 per cent. The deposits are close to the surface, and naturally vary a little in composition in different places. R. F. Blake aud V. l'Olivier's, and L. Dieulafait's analyses [5] of costra and caliche show:

	$NaNO_3$	KNO_3	NaCl	Na_2SO_4	$CaSO_4$	$MgCl_2$	$CaCO_3$
Caliche . .	37·9–62·3	0·3–26·1	20·6–41·5	2·7–7·3	0–64	0·4–0·7	0·1–0·15
Costra . .	18·6–24·1	6·45	22·0–57·5	3·5–16·6	7·79	0·4–1·6	0·09

In addition, the caliche contains 0·04–1·06 per cent. of potassium iodate, and the costra 0·03 per cent.; the caliche 0·02–1·32 of potassium chlorate. A. T. Machattie gives from 0·73 to 1·90 per cent. of sodium iodate in caliche, and R. F. Blake and V. l'Olivier a trace of iodine. L. Dieulafait found traces of lithium, rubidium, and cæsium salt; H. Beckurts, chlorates and perchlorates up to 5·64 per cent.; M. Märcker, borates and humus; C. F. Schönbein, nitrites and ammonia; R. Wagner, iodine and bromine. H. Grüneberg says the former is present as iodate or periodate. W. Ostwald considers that the presence of the highly oxidized salts—iodates and perchlorates—shows that the deposits were formed in an atm. highly charged with ozone. H. Guyard says the yellow coloration of some samples is due to the presence of potassium chromate; and the violet to manganese nitrate. The

unusual mineral species, *darapskite*, $NaNO_3.Na_2SO_4.H_2O$; and *nitroglauberite*, $6NaNO_3.2Na_2SO_4.3H_2O$, have also been reported by G. E. Bailey to be associated with the nitrate beds in Chili and California.

The extraction of sodium nitrate.—The caliche is mined by boring down to the lowest stratum. The bore is enlarged and charged with blasting powder. The explosion breaks up the nitre bed within a 50 ft. radius of the explosion. The caliche is sorted out and transported to the leaching works. The caliche is extracted with water, by the counter-current process used in the alkali industry, and the soln. is recrystallized so as to separate the sodium nitrate from the accompanying impurities—sodium chloride, sodium and calcium sulphates, sodium iodate, sodium perchlorate, insoluble matter, etc. Commercial *Chili saltpetre contains from 95 to 98 per cent. of sodium nitrate.* The sodium iodate which accumulates in the mother liquid is used for the manufacture of iodine. A. W. Allen has also described a process of treatment. C. M. Barton [6] has shown that by evaporating the liquor from the crystallizing vats to a great density, sodium nitrate with 25 per cent. potassium nitrate can be obtained. A bibliography has been published by A. Bertrand.

The world's consumption of sodium nitrate in 1912 was 2,460,000 tons; and in 1914, 2,633,000 tons. Sodium nitrate can be converted into potassium nitrate by double decomposition with potassium chloride,[7] with potassium hydroxide [8]; or with potassium carbonate; and also by first converting it into barium nitrate and

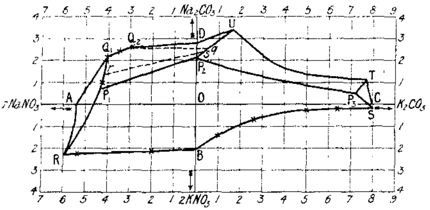

FIG. 76.—Solubilities of the Four Components of $2NaNO_3+K_2CO_3 \rightleftharpoons Na_2CO_3+2KNO_3$.

treating this product with potassium sulphate.[9] H. Hampel discussed the transformation of calcium nitrate into potassium nitrate: $K_2SO_4+Ca(NO_3)_2=2KNO_3+CaSO_4$. J. W. Brönsted showed that the free energy of the reaction $KCl+NaNO_3 \rightleftharpoons NaCl+KNO_3$ *is 740 cals.*

The double decomposition of sodium nitrate by potassium carbonate whereby sodium carbonate and potassium nitrate are formed, $2NaNO_3+K_2CO_3 \rightleftharpoons Na_2CO_3+2KNO_3$ is not a widely used technical process for converting sodium nitrate into the corresponding potassium salt; but its interest as an example of reciprocal salt formation led R. Kremann and A. Zitek [10] to investigate the conditions which give the maximum yields of potassium nitrate, and of sodium carbonate. There are the solubilities of the different salts to consider in the presence of one another, the transition points of the different hydrates, and the possible formation of complex salts—in the present case, the double salt, $Na_2CO_3.K_2CO_3.6H_2O$. R. Kremann and A. Zitek worked at 10° and 24·2°. The solubilities of the individual salts in mols. per 1000 grms. of water are plotted in Fig. 76. Here, *OD* represents the solubility of sodium carbonate; *OC*, of potassium carbonate; *OB*, of potassium nitrate; and *OA*, of sodium nitrate. The unit of measurement is that recommended by R. Kremann in his *Leitfaden der graphischen Chemie* (Berlin, 1910), namely, $2^{-\frac{1}{2}}$ less than that in space. R. Kremann and A. Zitek's values for the solubilities in mols. per litre are indicated in Table LVI, where "D.S." refers to the double salt, $K_2CO_3.Na_2CO_3.6H_2O$.

It might also be added that Na_2CO_3 is always present with the decahydrate in the solid phase at 10°.

TABLE LVI.—SOLUBILITIES OF POTASSIUM AND SODIUM NITRATES AND CARBONATES.

Solid phase. D.S. = double salt.	24·2°				10°			
	$2NaNO_3$	Na_2CO_3	K_2CO_3	$2KNO_3$	$2NaNO_3$	Na_2CO_3	K_2CO_3	$2KNO_3$
	SOLUTIONS SATURATED WITH ONE SALT.							
$NaNO_3$	5·37	—	—	—	4·730	—	—	—
$Na_2CO_3.10H_2O$	—	2·691	—	—	—	0·8247	—	—
K_2CO_3	—	—	—	—	—	—	7·838	—
KNO_3	—	—	—	1·86	—	—	—	1·497
	SOLUTIONS SATURATED WITH TWO SALTS.							
$NaNO_3+Na_2CO_3.7H_2O$	3·69	2·05	—	—	4·167	0·8247	—	—
$Na_2CO_3.7H_2O+Na_2CO_3.10H_2O$	2·701	2·482	—	—	separates out at 10°			—
Na_2CO_3+D.S.	—	3·422	1·760	—	—	1·663	2·561	—
K_2CO_3+D.S.	—	1·06	7·77	—	—	0·5767	7·61	
$K_2CO_3+KNO_3$	—	—	8·040	0·153	—	—	7·780	0·1316
$NaNO_3+KNO_3$	5·95	—	—	2·15	4·949	—	—	1·497
	SOLUTIONS SATURATED WITH THREE SALTS.							
$NaNO_3+Na_2CO_3+KNO_3$	4·165	2·055	—	1·400	4·479	0·619	—	1·069
$KNO_3+Na_2CO_3$+D.S.	—	3·695	0·184	1·053	—	1·513	0·1334	0·7057
$K_2CO_3+KNO_3$+D.S.	—	0·734	7·338	0·312	—	0·4981	7·408	0·0715

Again referring to Fig. 76, from the point *D*, the solubility of sodium carbonate decreases proportionally with increasing conc. of sodium nitrate, so that decahydrated sodium carbonate, $Na_2CO_3.10H_2O$, is precipitated along DQ_2; at Q_2 the decahydrate is transformed into the heptahydrate, $Na_2CO_3.7H_2O$; along Q_2Q_1, the heptahydrate is precipitated: at Q_1, the soln. is sat. with both the heptahydrate and sodium nitrate, $NaNO_3$: and the curve Q_1A represents the solubility of heptahydrated sodium carbonate and sodium nitrate. The addition of sodium nitrate to a soln. of potassium nitrate or of potassium nitrate to one of sodium nitrate raises the solubility of the other as shown by the curves *AR*, and *RB*, where *R* represents a soln. sat. with respect to both salts. This is a case where salts with a common ion do not mutually lower but rather raise one another's solubility. A double salt has not been isolated, and the phenomenon is accordingly ascribed to the formation of complex ions. The curve *BSC* represents the effect of potassium carbonate on the solubility of potassium nitrate, and *vice versâ*; *S* represents a soln. sat. with both these salts. The curve *DUTC* represents the effect of potassium carbonate on the solubility of sodium carbonate; at *U* the soln. is sat. with sodium carbonate and the double salt, $Na_2CO_3.K_2CO_3.6H_2O$, and at *T*, with potassium carbonate and the double salt. Owing to the formation of the double salt, there are three soln. sat. with three salts, namely, P_1, sat. with the two nitrates and sodium carbonate; P_2, with potassium nitrate, the double salt, and sodium carbonate; and P_3, with potassium nitrate, the double salt, and potassium carbonate. The line Q_1P_1 represents a soln. sat. with sodium nitrate and carbonate with the addition of increasing proportions of potassium nitrate; RP_1, of the two nitrates, with additions of sodium carbonate; UP_2, of the double salt and sodium carbonate, with potassium nitrate; TP_3, the double salt and potassium carbonate, with potassium nitrate; SP_3, with potassium nitrate and carbonate, with the double salt; P_1P_2, of sodium carbonate and potassium nitrate, with sodium nitrate; and P_2P_3, with the double

salt and potassium nitrate, with additions of sodium carbonate. The regions bounded by these lines are RAQ_1P_1, representing soln. sat. with respect to sodium nitrate ; $RP_1P_2P_3SB$, potassium nitrate ; SP_3CT, potassium carbonate ; TP_3P_2U, the double salt ; and $UP_2P_1Q_1Q_2D$, sodium carbonate. The latter is present as the decahydrate in the whole field $P_1Q_1Q_2DUP_2$, but at 24·2°, the field is subdivided into three regions : Q_2DUq, with the decahydrate, Na_2CO_3, as solid phase ; Q_2Q_1rsq, with the heptahydrate, $Na_2CO_3.7H_2O$, as solid phase ; and rsP_2Q_1, with the monohydrate, $Na_2CO_3.H_2O$, as solid phase. The soln. along P_1P_2 is sat. with KNO_3 and with monohydrated sodium carbonate as solid phase. The points r, q, and s are arbitrarily selected—the observed facts are the transition point Q_2, and the fact that the monohydrate separates along the line P_1P_2. The transition point of the monohydrate is at 37°, and this point is lowered by the presence of the large amount of salt corresponding with P_1P_2 that the monohydrate separates along the line P_1P_2. In the technical application of the process, the sodium nitrate and potassium carbonate are brought together at a suitable conc., and after the precipitation of potassium nitrate there remains a soln. sat. with potassium nitrate in the presence of two other salts in soln. At 24·2°, a soln. will be obtained corresponding with a point in the region $RSBP_1P_2P_3$, and the actual position will be determined by the conc. of the soln. of sodium nitrate and potassium carbonate initially employed, and the conditions can be so chosen that the resulting soln. is represented by a point lying on P_1P_2, and after the precipitation of potassium carbonate the soln. will then be sat. with sodium carbonate. Let U_K denote coeff. of efficiency, that is, the percentage of potassium carbonate used up, and U_{Na} the corresponding coeff. of efficiency for the sodium, then

$$U_K=\frac{100[CO_3-K_2]}{CO_3}\ ; \text{ and } U_{Na}=\frac{100[Na_2-(NO_3)_2]}{Na_2}$$

Since all the CO_3 and K_2 in the soln. comes from the potassium carbonate, it follows that the term $[CO_3-K_2]$ is eq. to the potassium precipitated as solid nitrate, and U_K therefore represents this amount as a percentage on the original potassium taken. Similarly, U_{Na} gives the percentage of the radicle NO_3 which is precipitated, and since Na_2 is eq. to $(NO_3)_2$, it also gives the percentage of sodium usefully employed for the production of potassium nitrate. In continuing their study, R. Kremann and A. Zitek point out that in practice it is desirable to obtain a soln. as sat. as possible with sodium carbonate after the precipitation of the potassium nitrate, so that the mother liquor can be worked as economically as possible for sodium carbonate. Hence, the amounts of the two original salts employed will be those required for the soln. to be sat. with sodium carbonate after the precipitation of potassium nitrate. The conc. of soln. sat. with both sodium carbonate and potassium nitrate is represented by a point on the curve P_1P_2. The coeff. of efficiency for soln. represented by the points P_1, P_2, and P_3 are :

	P_1	Between P_1P_2	P_2	Near P_3	P_3
U_K . . .	31·7	67·1	67·6	46·8	6·8
U_{Na} . . .	8·6	64·5	68·0	30·3	78·4

The maximum efficiency is clearly at the point P_2, for the potassium efficiency decreases in passing towards P_3. A mixture containing 29·5 grms. of sodium nitrate, 24·5 potassium carbonate, and 50 grms. of water, after agitation, furnishes a soln. corresponding with the point P_2, and there separates 24·1 grms. of potassium nitrate contaminated with 4·5 per cent. of carbonate—the theoretical yield is 23·6 of potassium nitrate.

Sodium carbonate is obtained by adding sodium nitrate to the mother liquid which after the separation of the potassium nitrate corresponded with P_2 ; this carries the point representing the composition of the soln. along P_2P_1 towards P_1. At P_2 there is practically no sodium nitrate in soln., and when this salt is added, the solubility of the sodium carbonate is lowered, from 37·7 grms. per litre

at P_2 to 21·7 grms. per litre at P_1, and this salt is therefore precipitated. Potassium nitrate is not precipitated because its solubility rises towards P_1. To get a soln. corresponding with P_1, after the precipitation of the sodium carbonate, it is necessary to add potassium carbonate which reacts with the sodium nitrate present in large excess, forming sodium carbonate and potassium nitrate. The former salt is precipitated, the latter remains saturating the soln. The difference in the solubility of sodium carbonate at P_2 and P_1 is 160 grms. per litre, and what is virtually a theoretical yield can be obtained. R. Kremann and A. Zitek also found that it was better to work at 24·2° than at 10° because the coeff. for the initial conc. at the latter temp. are smaller.

The usual process of converting sodium into potassium nitrate is as follows: Chili saltpetre is dissolved in about 1½ times its weight of boiling water, and a soln. of sylvine—potassium chloride, from the Stassfurt deposits—in three times its weight of water, is poured into the sodium nitrate soln. Sodium chloride at once separates as a fine granular precipitate: $KCl+NaNO_3 \rightleftharpoons NaCl+KNO_3$. The crystals are removed, and the mother liquid is evaporated to about half its original volume, and the sodium chloride again removed. The sodium chloride is washed with water to recover some of the potassium nitrate removed with the crystals, and the washings used for dissolving more of the raw material. The mother liquid is further conc. by evaporation. Crude nitre crystallizes from the soln. This is purified by recrystallization from boiling water, which is stirred while cooling so that the nitre crystals may be small and granular—*nitre meal*. The crystals are dried and packed in sacks for transport. The potash nitre still holds about half per cent. of sodium chloride. The by-product, sodium chloride—*pickling salt*—is preferred to ordinary salt for pickling meat, probably because of the quantity of nitre it still contains.

The origin of the nitre beds is not known.[11] It is generally agreed that the nitrogen is of organic origin—animal or vegetable. Since immense deposits of guano have been found on some of the islands off the coast of Peru—*e.g.* the Chincha Islands—it has been suggested that the nitrogen is derived from the guano. If so, it is not clear where the phosphates have gone, since there is practically no calcium phosphate in the nitre beds. Of course, the soluble nitrates may have been leached from decayed guano in some other locality and deposited in their present form. The origin of the deposits has not been satisfactorily solved. The most generally accepted explanation is that the beds have resulted from the decay of enormous quantities of organic matter, particularly seaweed, which probably accumulated in a long narrow lagoon of water. This deposit was afterwards elevated by movements of the earth. The geologists claim to recognize the remains of seaweed in some parts of the nitre beds.

When organic matter decays, say, in the soil of cattle yards and stables, ammonia and ammonium compounds are produced by the action of certain bacteria. If the soil be fairly dry, but not too dry, a white scum appears on the exposed surface. The scum is made up of small crystals of potassium nitrate; and, after a time, if the soil be extracted with water and strained, the liquid, on evaporation, furnishes yellowish-brown crystals of crude nitre. The crude nitre can be purified by resolution and crystallization. The white efflorescence sometimes seen on the walls of stables, etc., is sometimes, though not always, due to the formation of nitrates in this way.

The first stage in the decomposition of the organic matter is due to the action of certain bacteria. Ammonia and ammonium compounds are formed along with other gases which produce the characteristic odour of putrefaction. The next stage in the process of decomposition is due to the action of a special bacterium—**the nitrous ferment**—which converts the ammonia into nitrous acid: $2NH_3+3O_2 = 2H_2O+2HNO_2$. Another bacterinm—**the nitric ferment**—transforms the nitrous into nitric acid: $2HNO_2+O_2=2HNO_3$. The two last-named varieties were isolated by S. Winogradsky[12] in 1891. By the agency of these three types of bacteria, the soil is constantly receiving fresh supplies of nitrates necessary for the growth of plants, and derived from the decomposition of the organic matter present in the soil. The free acids are not really present in the soil because the alkali or alkaline

earths present interact with the acids producing the nitrates and nitrites. It is owing to these reactions that water, contaminated by drainage from surface soil, contains nitrates. According to S. von Bazarewsky, the nitrate formation in soils extends down to a depth of 10 cm., and the optimum temp. is between 25° and 27°.

During the Napoleonic wars, France had great difficulty in procuring sufficient nitre for the manufacture of gunpowder. This led to the construction of **nitre beds** or **nitre plantations** in various parts of the country.[13] When the French ports were thrown open, after these wars, the manufacture of nitre, in France, was abandoned because it could be imported more cheaply from India. The process is still used in a few localities—*e.g.* Sweden.

Soil rich in humus, dung, or animal offal is piled into heaps with the *débris* from buildings, or with lime, or wood ashes. The heaps are protected from rain by sheds. A system of gutters or pipes may also distribute the liquid excretions of animals over the top of the heap. The piled mass is called a nitre plantation. Before long a white film of nitre "grows" on the windward face of the pile. This is scraped off regularly, and leached as indicated above. If lime be present, the resulting calcium nitrate is converted into potassium nitrate by the addition of wood ashes—potassium carbonate: $Ca(NO_3)_2+K_2CO_3=2KNO_3+CaCO_3$. The nitre is then purified by recrystallization.

In the hot dry countries of the East—India, Persia, Arabia—Guatemala, etc., particularly in the neighbourhood of villages—old or new—where urine and other organic matters find their way into the calcareous soil owing to imperfect systems of sewage disposal, the process of nitrification goes on rapidly. The soil or nitrate earth, called *chhilua*, is extracted with water every few years, and the nitrates, chiefly calcium and potassium nitrate, are extracted as indicated above.[14] The product from the soil in the Valley of the Ganges (Bengal) is called *Bengal saltpetre*; it is principally potassium nitrate. If calcium nitrate be present, potassium carbonate is added to the aq. extract from the soil, so that calcium carbonate may be precipitated, and potassium nitrate remain in soln. The Indian term for nitre is *sora*, and the men who collect the raw material are called sorawallahs. The nitre so collected was exported and, prior to the introduction of cheap ice-machines, was used as a freezing mixture. The nitrates of lithium, rubidium, and cæsium are made by the crystallization of the soln. obtained by neutralizing a soln. of nitric acid with the respective carbonates or hydroxides.

Crystalline form.—Lithium nitrate crystallizes in rhombohedra (trigonal system).[15] P. W. Bridgman observed no new form of lithium nitrate between 20° and 200°, and press. between 1 and 12,000 kgrms. per sp. cm. The older authorities—*e.g.* P. Kremers—supposed this salt to be trimorphic, but the supposed polymorphism is probably due to their mistaking hydrates for polymers of the anhydrous salt. It is doubtful if lithium nitrate is isomorphous with silver or sodium nitrate, although J. W. Retgers says that sodium and lithium nitrates are isomorphous.

Sodium nitrate forms trigonal crystals[16] with the axial ratio $a:c=1:0{\cdot}8297$. The rhombohedral form of the crystals of sodium nitrate explains why this salt is sometimes called *cubic nitre*, or *rhombohedral nitre*, as distinct from *prismatic nitre*, or potassium nitrate. The crystals illustrated in Fig. 78 have been crystallized on a slip of glass, and photographed under the microscope. The outline drawing shows the form of an idealized crystal, and both salts, according to A. des Cloizeaux, have a strong negative double refraction. The crystals of lithium and sodium nitrates resemble one another so closely that they appear to be isomorphous, but R. Krickmeyer found that at 60°, when crystals of anhydrous lithium nitrate are formed, soln. containing different proportions of the two salts give crystals of sodium nitrate quite free from the lithium salt. The crystals of sodium nitrate closely resemble those of calcite in their angular measurements and optical properties, so that in spite of the difference in the composition of these two salts, they have long been regarded as isomorphous. If a freshly cleaved crystal of calcite be placed in a crystallizing soln. of sodium nitrate, the rhombohedra of the nitrate

orient themselves so that their edges are parallel to those of the calcite cleavage; but the deposition is not regular on old cleavage faces of the calcite. T. V. Barker showed that the parallel deposition of sodium nitrate on clean and fresh cleavage faces of the calcite is independent of the habit or variety of the calcite; and after studying many examples of the phenomena, he concluded that the necessary condition for parallel and regular growth is closeness of mol. volume rather than similarity of angle or of axial ratio. H. A. Miers and J. Chevalier also showed that fragments of calcite will serve for inaugurating the crystallization of undercooled soln. of sodium nitrate.

Sodium nitrate, although so like the other alkali nitrates which furnish polymorphic forms, has not yet presented polymorphic forms. Trigonal sodium nitrate crystallizes isomorphously with the high temp. form of silver nitrate, and in small percentages with the low temp. form, so that the two salts appear isodimorphous. Mixed soln. furnish rhombic mixed crystals if silver nitrate be in excess, and trigonal crystals if the sodium salt be in excess. D. J. Hissink tried to find a second modification of sodium nitrate between $-50°$ and $270°$; P. W. Bridgman also sought for the suspected second modification of sodium nitrate between $20°$ and $200°$, and 1 and 12,000 kgrms. per sq. cm. press. Negative results were obtained; it is assumed by analogy with silver nitrate that the second modification will be stable at a low temp. at atm. press., and the transition temp. will fall with rising press. R. W. G. Wyckoff found the **X-radiogram** of trigonal sodium nitrate corresponded with a body-centred lattice containing two mols. of $NaNO_3$. The marshalling of the atoms in the crystal as a whole resembles that within a crystal of sodium chloride with NO_3-groups replacing the Cl-atoms of NaCl. The length of the side of the unit rhombohedron is $6·065\times10^{-8}$ cm., and the angle between the axes $47° 14'$.

It is interesting to watch the crystallization of a drop of a slightly supersaturated, warm soln. of potassium nitrate on a glass slip under the microscope. Crystallization starts at the edges. Here, rhombohedral crystalline [17] plates (left, Fig. 78) are first formed with axial ratios: $a:b:c=0·5910:1:0·7011$; these are quickly followed by needle-like rhombic crystals. As a matter of fact, both forms of crystals appear in the photograph (left, Fig. 78). Immediately the rhombohedral crystals touch the rhombic crystals, the former lose their sharp outlines, and needle-like rhombic crystals sprout forth on all sides. Hence, as M. L. Frankenheim [18] showed in 1837, *potassium nitrate is dimorphous*. The rhombic crystals are unstable above, and stable below, 129°; and, conversely, the rhombohedral crystals are stable above, and unstable below, 129°. Hence, 129° is a transition temp.:

$$\text{Potas. nitrate}_{\text{rhombic}} \overset{129°}{\rightleftharpoons} \text{Potas. nitrate}_{\text{rhombohedral}}$$

The reported values for the transition point vary from the 126° of F. Wallerant to the 130° of M. Bellati and R. Romanese. The rhombohedral crystals which are stable above 129°, appear in two forms: α-KNO_3 separates from the molten flux on cooling in strongly negative doubly refracting rhombohedra, and, if undercooled to 114°, below the transition point into the rhombic form, they suffer an abrupt increase in their double refraction, and pass into the β-variety, which consists of crystals with one optic axis parallel to that of the α-rhombohedral form. The crystals of potassium and sodium nitrates separate independently from a mixed aq. soln., and the hexagonal crystals of sodium nitrate which separate contain but a fraction of a per cent. of the potassium salt, and the rhombic crystals of potassium nitrate, a fraction of a per cent. of the sodium salt. D. J. Hissink says that mixed crystals separate from a molten mixture with less than 24 and more than 85 per cent. of potassium nitrate; he also observed a lowering of the transition point from the rhombohedral to the rhombic crystals in the presence of sodium nitrate, so that with six per cent. of the sodium salt no transformation

occurs. There may be an intermixture of crystals of the rhombohedral salt which, says P. Groth, is not a true isomorphous mixture.

P. W. Bridgman gave the equilibrium diagram shown in Fig. 77 for the polymorphic forms of potassium nitrate; and the various transition temp. shown in Table LVII are selected from his values. For the triple point II–III–IV, at 21·3° and 2930 kgrms. per sq. cm. press., the change in vol. from II–III is 0·01560; III–IV, 0·02840; and II–IV, 0·04400 c.c. per grm., and the corresponding latent heats are 0·533, 2·166, and 1·613 kgrm.-m. per grm. For the triple point I–II–III, at 128·3° and 115 k.-grm. per sq. cm. press., the change in vol. from I–III is 0·01420; II–III, 0·00886; and I–II, 0·00534 c.c. per grm., while the corresponding latent heats are 2·631, 1·778, and 4·409. No other forms were observed between 20° and 200° up to 12,000 kgrms. per sq. cm. press.

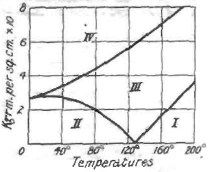

FIG. 77.—Effect of Pressure on the Transition Temperature of Potassium Nitrate (Diagrammatic).

Rubidium nitrate forms rhombic bipyramidal (*pseudo-hexagonal*) *crystals with axial ratios* $a:b:c$ $=1·7366:1:0·7108$, which were formerly thought to be hexagonal.[19] Similar remarks apply to cæsium nitrate. Rubidium nitrate is trimorphous, cæsium nitrate dimorphous. The crystals of rubidium nitrate have a feeble positive double refraction, and, according to W. Schwarz, pass at 161·4° into a singly refracting variety belonging to the cubic system, and which, at 219°, pass into another negative doubly refracting variety which is stable up to the m.p. *Cæsium nitrate does not give the negatively doubly refracting variety*, but after solidification, this salt is singly refracting and cubic down to 161°, when it passes into the pseudo-hexagonal form with a feeble positive double refraction.

F. Wallerant found that when mixed crystals are formed with increasing proportions of rubidium nitrate, the transformation point of cæsium nitrate was lowered from 161°, until, with 75 per cent. of $RbNO_3$, it reaches 145°; the transition

TABLE LVII.—THE EFFECT OF PRESSURE ON THE TRANSITION TEMPERATURES OF POTASSIUM NITRATE.

Press.		Transition temp.	Changes in vol. c.c. per grm.	Latent heat kgrm. m. per grm.
I–III	1	125·8°	0·01424	2·609
	2000	167·7°	0·01370	2·964
	4000	207·9°	0·01354	3·264
I–II	1	127·7°	0·0060	4·95
II–III	510	120·0°	0·01050	1·867
	2350	60·0°	0·01480	0·968
	2955	20·0°	0·01560	0·544
II–IV	2665	0°	0·04470	1·522
	5000	96·8°	0·02680	1·543
	9000	214·5°	0·02500	2·936

point then rises with increasing proportions of rubidium nitrate. Rubidium nitrate forms with potassium nitrate mixed crystals resembling the latter unless the soln. contains over $RbNO_3:KNO_3=6:3$, when the crystals are pseudo-hexagonal. F. Wallerant has studied the formation of mixed crystals of cæsium or rubidium nitrate with potassium nitrate by melting the two salts together. T. V. Barker failed to obtain parallel growths of the rhombohedral modification of potassium nitrate on calcite, although he obtained the rhombohedral *form of the nitrate from* crystallizing drops of a soln. of the salt. When the growth of the rhombohedra has gone on for some time, the crystals rapidly pass into a crystalline aggregate

of the stable rhombic form. P. W. Bridgman represented the effect of press., expressed in atm., on the transition point of rubidium nitrate by Fig. 79, and

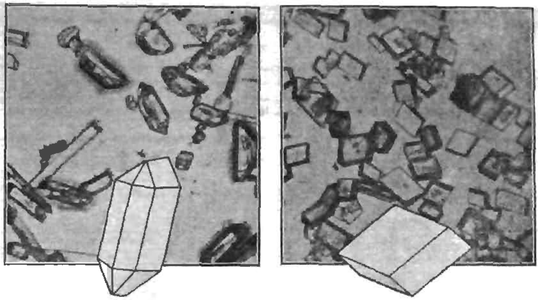

Fig. 78.—Potassium Nitrate (left) and Sodium Nitrate (right) Crystals.

on cæsium nitrate by Fig. 80, and by data from which Table LVIII is selected. No other forms were observed with press. up to 12,000 kgrms. per sq. cm. between

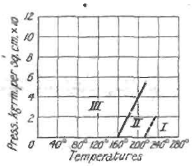

Fig. 79.—Effect of Pressure on the Transition Temperature of Rubidium Nitrate.

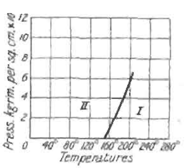

Fig. 80.—Effect of Pressure on the Transition Temperature of Cæsium Nitrate.

20° and 200°. The phases which are analogous are numbered alike in the phase diagrams of rubidium and cæsium nitrates, Figs. 79 and 80. The crystalloluminescence of potassium nitrate has been studied by E. Bandrowsky.

Table LVIII.—The Effect of Pressure on the Transition Temperatures of Rubidium and Cæsium Nitrates.

Press.	Rubidium nitrate.			Cæsium nitrate.		
	Transition temp.	Change of vol. c.c. per grm.	Latent heat kgrm. m. per grm.	Transition temp.	Change of vol. c.c. per grm.	Latent heat kgrm. m. per grm.
1	164·4°	0·00688	3·04	153·7°	0·00405	1·820
1000	174·1°	0·00646	3·03	163·1°	0·00387	1·776
4000	201·4°	0·00518	2·80	190·1°	0·00334	1·644
6000	218·6°	0·00434	2·53	207·1°	0·00298	1·545

The **specific gravity** of anhydrous lithium nitrate is 2·334 (17·5°), according to P. Kremers;[20] and 2·442 (115°), according to L. Troost. For sodium nitrate, values ranging from 2·09 to 2·29 have been published; the older values are too low—

F. L. Haigh give 2·266 (20°); J. W. Retgers, 2·265 (15°). According to R. Lorenz, a cubic centimetre of the molten salt weighs 2·12—0·0007θ grms. at a temp. θ° between 320° and 515°. G. Quincke gives the sp. gr. 2·26 at 0°, 1·878 at the m.p., and 1·84 at 350°. For potassium nitrate numbers ranging from 2·086 to 2·143 have been published. In 1690, R. Boyle gave 1·900. The more recent values are 2·109 (16°) by J. W. Retgers, 2·109 (20°) by F. L. Haigh. M. Bellati and L. Finazzi give 2·1104 (0°), 2·1037 (17·25°), 2·0949 (40·05°), 2·0784 (77·20°), 2·0607 (114·5°), 2·0330 (130·6°), and 2·0199 (154·4°). J. W. Retgers obtained 3·131 for rubidium nitrate; and T. W. Richards and E. H. Archibald, 3·687 for cæsium nitrate. The following may be taken as the best representative values; those for the rubidium and cæsium salts are by F. L. Haigh:

	$LiNO_3$	$NaNO_3$	KNO	$RbNO_3$	$CsNO_3$
Sp. gr.	2·388	2·267	2·10	3·112	3·643
Mol. vol.	28·8	41·9	48·5	47·1	52·8

F. M. Jäger's values for the sp. gr. of the molten alkali nitrates are indicated in Table LIX; for lithium nitrate at θ°, the sp. gr. D, water at 4° unity, is D=1·755—0·000546(θ—300); sodium nitrate, D=1·914—0·0006719(θ—300); potassium nitrate, D=1·898—0·0007652(θ—300); rubidium nitrate, D=2·492—0·000972(θ—300); and cæsium nitrate, D=2·824—0·001114(θ—400). R. Lorenz and co-workers gave for fused potassium nitrate, D=2·044—0·006θ, and for fused sodium nitrate, D=2·12—0·0007θ. C. Sandonnini studied the sp. gr. of mixtures of sodium and potassium nitrates.

According to W. C. Röntgen and J. Schneider,[21] the mol. **compressibility** of soln. of the alkali nitrates with a molecule of the salt per 700 and 1500 mols. of water is:

	HNO_3	NH_4NO_3	$LiNO_3$	KNO_3	$NaNO_3$
$700H_2O$	0·981	0·954	0·934	0·930	0·922
$1500H_2O$	0·958	0·908	0·870	0·863	0·853

The **capillary constant** [22] of molten sodium nitrate, a^2=8·55 sq. mm.; and of potassium nitrate, a^2=8·35 sq. mm. The **surface tension** of sodium nitrate is 78·8 dynes per sq. cm., and of potassium nitrate 69·8 dynes per cm. The change of the capillary rise of molten potassium and sodium nitrates, or the variation of the mol. surface energy with temp., led J. F. Bottomley to assume that in the molten state, the molecules of these salts form complexes containing nine or ten simple molecules—$(KNO_3)_{9-10}$ or $(NaNO_3)_{9-10}$. The **compressibilities** of aq. soln. of lithium, sodium, and potassium nitrates of different conc. have been measured by W. C. Röntgen and J. Schneider, and F. Pohl; of sodium nitrate by H. Gilbault. F. M. Jäger's values for the surface tension (dynes per cm.), sp. gr., and mol. **surface energy** (ergs. per sq. cm.) are indicated in Table LIX. T. Martini, and G. Wertheim

TABLE LIX.—SPECIFIC GRAVITIES AND SURFACE TENSION OF MOLTEN ALKALI NITRATES.

	Temp.	Surface tension.	Sp. gr.	Surface energy.	Temp. coeff. per degree.
$LiNO_3$	358·5°	111·5	1·723	1304·5	0·45
	609·4°	96·2	1·586	1189·4	0·45
$NaNO_3$	321·5°	119·7	1·900	1508·6	0·24
	738·2°	93·7	1·620	1313·3	0·61
KNO_3	380°	110·4	1·837	1597	0·52
	771·6°	80·2	1·537	1307	0·85
$RbNO_3$	326·5°	107·5	2·467	1643·4	0·78
	726·2°	77·7	2·078	1331·8	0·78
$CsNO_3$	425·5°	91·8	2·796	1534·4	0·42
	686·4°	72·5	2·505	1321·0	0·42

have measured the **velocity of sound** in soln. of sodium and potassium carbonate. The **viscosity** of molten sodium nitrate [23] at 308° is 0·02909; 356°, 0·02284; at

406°, 0·01780; and at 495°, 0·01321; for potassium nitrate, at 333°, 0·02970; at 393°, 0·02216; and at 506°, 0·01344. According to C. E. Fawsitt, at the eutectic temp. of a mixture of potassium and sodium nitrates, the viscosity is a *maximum*. P. B. Davis and H. I. Johnson have studied the viscosity of soln. of the alkali *nitrates in formamide, ethyl alcohol, and in glycerol*.

S. Arrhenius, K. Mützel, and R. Reyher found the viscosity of N-, $\frac{1}{2}N$-, $\frac{1}{4}N$-, and $\frac{1}{8}N$-soln. of sodium nitrate to be respectively 1·0655, 1·0259, 1·0122, and 1·0069, and for soln. of potassium nitrate, at 21°, respectively 0·9758, 0·9822, 0·9870, and 0·9921 (water unity). According to J. D. R. Scheffer,[24] the **coefficient of diffusion** of $1·255N$- and $0·220N$- soln. of *potassium nitrate* at 25° is 0·57 and 0·62 respectively; and for $1·375N$- and $0·122N$-soln. at 13°, respectively 0·77 and 0·90. For potassium nitrate, at 17·6, J. Thovert found with $3·9N$- and $0·02N$-soln. diffusion coeff. of 0·89 and 1·28 sq. cm. per day respectively.

The **melting point** of lithium nitrate, according to T. Carnelley,[25] is 267°, and according to H. R. Carveth, 253°. For sodium nitrate *numbers ranging from* R. Lorenz and his co-workers' 310° to H. R. Carveth's 318° have been reported. For potassium nitrate, the numbers range from 334·5° to 246·3°. H. W. B. Roozeboom gives 334°. According to F. L. Haigh, rubidium nitrate melts at 313°; and cæsium nitrate at 407°; T. W. Richards and E. H. Archibald give 414°. The following are representative values:

	$LiNO_3$	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$
M.p. . . .	261°	306·8°	334·5°	313°	414°

It will be observed that the m.p. of rubidium nitrate is lower than that of potassium nitrate, while that of cæsium nitrate is higher. This is an unusual sequence in the properties of the alkali salts—see the solubilities for another irregularity. H. R. Carveth found a eutectic with 54·5 per cent. of KNO_3 and 45·5 per cent. of $NaNO_3$, at 218°; with 66 per cent. of KNO_3 and 34 per cent. of $LiNO_3$ at 129°; and with 53 per cent. of $NaNO_3$ and 47 per cent. of $LiNO_3$ at 204°. H. R. Carveth *also* studied the fusion point curves of ternary mixtures of lithium, sodium, and potassium nitrates. These three salts form homogeneous soln., and there is no sign of the formation of solid soln., mixed crystals, or double salts. The fusion points of binary mixtures of these salts are represented by points on the boundary lines of the triangle, Fig. 81; the pure salts by the apices of the triangle, and ternary mixtures by points inside the triangle. The binary eutectics are represented by *A*, *B*, and *C*, and, in accord with A. C. van Rijn van Alkemade's theorem, for systems of this type: *In passing from the binary eutectic to the ternary eutectic there is a fall of temperatures*, is illustrated by the fact that the three binary eutectic temp. are 218°, 129°, and 204°, while the ternary eutectic temp. is nearly 119°. F. Guthrie has also studied the ternary system: $NaNO_3$—KNO_3—$Pb(NO_3)_2$, and the ternary system: KNO_3—KCl—H_2O; A. W. C. Menzies and N. N. Dutt, *the ternary system* KNO_3—$NaNO_3$—$Ca(NO_3)_2$; and W. D Harkins and G. L. Clark, of KNO_3—$NaNO_3$—$Ba(NO_3)_2$; and KNO_3—$LiNO_3$—$Ba(NO_3)_2$.

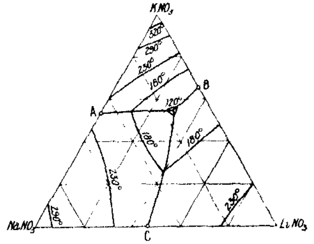

FIG. 81.—Fusion Curves of the Ternary System: $LiNO_3$—$NaNO_3$—KNO_3.

M. Bellati and L. Finazzi give 0·000191 for the **coefficient of cubical expansion** of solid potassium nitrate at 20°, and between 6·8° and 121·9°, $v=v_0(1+0·0001818\theta+0·000000256\theta^2)$ and between 130·5° and 154·4°,

$v=v_0(1+0{\cdot}00028060\theta)$. The coeff. of thermal expansion (cubical) of aq. soln. of lithium nitrate, according to C. Forch, for soln. with 34·5 grms. per litre 0·000070 (0°–5°), 0·000127 (5°–10°), and 0·000392 (35°–40°); for soln. with 69 grms. of salt per litre these numbers are respectively 0·000145 (0°–5°), 0·000190 (5°–10°), and 0·000412 (35°–40°); and for soln. with 138 grms. per litre, 0·000261 (0°–5°), 0·000289 (5°–10°), and 0·000449 (34°–40°). For soln. of sodium nitrate with 42·5 grms. per litre 0·000114 (0°–5°), 0·000169 (5°–10°), and 0·000416 (35°–40°); for soln. with 85 grms. per litre, 0·000204 (0°–5°), 0·000253 (5°–10°), and 0·000446 (35°–45°); and for soln. with 170 grms. per litre, 0·000349 (0°–5°), 0·000372 (5°–10°), 0·000507 (35°–45°). Similarly, for soln. of potassium nitrate with 45·5 grms. per litre, 0·000099 (0°–5°), 0·000155 (5°–10°), and 0·000407 (35°–40°); and for soln. with 91 grms. per litre, 0·000183 (0°–5°), 0·000223 (5°–10°), and 0·000430 (35°–40°). F. L. Haigh gives for the expansion of soln. of the alkali nitrates when the expansion at 20° is the standard of reference:

	$LiNO_3$	NH_4NO_3	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$
20°–0°	−42·1	−43·1	−52·4	−48·2	−49·5	—
20°–10°	−25·3	−25·7	−31·0	−28·3	−29·0	—
20°–30°	33·4	34·4	38·4	35·5	36·0	36·1
20°–40°	73·1	72·1	82·9	78·8	78·9	79·5
20°–50°	118·6	120·2	132·0	127·2	127·4	127·7

G. Jäger[26] gives the **heat conductivity** of 20 and 44 per cent. sodium nitrate soln. as 94·9 with 90·4 respectively—silver unity—and for 10 and 20 per cent. soln. of potassium nitrate, 97·2 and 92·2 respectively. According to C. C. Person, the **latent heat of fusion** of sodium nitrate is 5·355 Cals. per mol. at 310·5°; and of potassium nitrate 4·79 Cals. per mol. at 339°. K. M. Goodwin and H. T. Kalmus' value for potassium nitrate is 2·57 cals. at 333°. According to M. Bellati and R. Romanese, the heat of transition from the rhombohedral to the rhombic form is 11·89 cals.; P. W. Bridgman, 11·6 cals.—*vide supra*.

According to J. H. Schüller,[27] **the specific heat** of sodium nitrate is 0·2650 between 27° and 59°; according to H. V. Regnault, 0·2782 between 41° and 98°; according to C. C. Person, 0·41 between 320° and 430°; and, according to K. M. Goodwin and H. T. Kalmus, 0·388 between 235° and 333°, and 0·430 between 333° and 367°. For potassium nitrate, H. Kopp's value is 0·232 between 14° and 45°; H. V. Regnault's, 0·2388 between 13° and 98°; K. M. Goodwin and H. T. Kalmus', 0·292 between 240° and 308°, and 0·333 between 308° and 411°; and C. C. Person's value for the molten salt between 350° and 435°, is 0·3319. The sp. ht. of aq. soln. of sodium nitrate in 10 mols. of water is 0·076; in 50 mols. of water, 0·918; and in 200 mols. of water, 0·975, at 18°. Similarly, for soln. of potassium nitrate with 25 mols. of water, the sp. ht. is 0·832; with 50 mols. of water, 0·901; and with 200 mols. of water, 0·966.

The **heat of formation** of lithium nitrate, $LiNO_3$, from its elements is 111·4 Cals.;[28] sodium nitrate, 111·25 to 110·7 Cals.; for potassium nitrate, 119 to 119·5 Cals. The **heat of solution** of lithium nitrate is, according to J. Thomsen, $LiNO_3$+aq, 0·3 Cal.; and of sodium nitrate in 200 mols. of water, −5·03 Cals.; M. Berthelot gives for the same salt with 235–470 mols. of water at 10°–15°, −4·7 Cals., and F. L. Haigh, −4·878 Cals. According to J. Thomsen, the heat of soln. of a mol. of potassium nitrate in 200 mols. of water is −8·52 Cals., and, according to M. Berthelot, −8·3 Cals. when in 280–560 mols. of water at 10°–15°. G. Staub, R. Scholz, and E. F. von Stakelberg have also measured the heat of soln. Q of potassium nitrate in water, and the latter gives for the decrease in the value of Q for n mol. of the salt in 100 grms. of water at 0°, Q=9550−1500n cals.; and at 15°, Q=9100−1337·5n+143·8n^2 cals. N. Galitzky has also studied the influence of alcohol on the heat of soln. of potassium nitrate in water, and found that a greater cooling occurs with alcoholic soln. than with water; the maximum occurs with between 20 and 30 parts alcohol for 100 of water. S. U. Pickering found the heat

of soln. of lithium nitrate in alcohol to be 4·66 Cals. The best representative values are:

	$LiNO_3$	$NaNO_3$	NH_4NO_3	KNO_3	$RbNO_3$	$CsNO_3$
Heat of soln. .	0·439	−4·878	−6·261	−8·374	−8·780	−9·603

F. R. Pratt has investigated the heat of dilution of potassium and sodium nitrates. J. Thomsen gives the **heat of neutralization**: $HNO_3+KOHaq=27·54$ Cals., and, according to M. Berthelot, when all are solid: $HNO_3+KOH=KNO_3+H_2O+42·2$ Cals.

The solubility of the alkali nitrates.—The alkali nitrates are all very soluble in water; lithium nitrate is peculiar in forming a number of hydrates, and in this respect it is related more with the alkaline earths than with the alkali family. P. Kremers[29] first noted the formation of a hydrate by this salt. Rhombohedral crystals were formed above 10°, crystalline needles below; the former were considered to be anhydrous, the latter a 2½-aquo-salt. L. Troost also confirmed P. Kremer's observations, and D. B. Dott showed, in 1893, that P. Kremer's 2½-hydrated salt is more probably a tri-hydrated salt, $LiNO_3.3H_2O$. The solubility data for lithium nitrate determined by P. Kremers do not agree very well with those of F. G. Donnan and B. C. Burt, probably because the earlier workers on the solubility of salts did not pay sufficient attention to securing complete saturation, and a constant temp. **Trihydrated lithium nitrate,** $LiNO_3.3H_2O$, crystallizes from aq. soln. at a temp. below 29·6°; above 29·6° and below 61·1°, **hemihydrated lithium nitrate,** $LiNO_3,\frac{1}{2}H_2O$, is formed; and above 61·1°, the anhydrous salt is the stable solid phase. The solubility of lithium nitrate is expressed as *grams of $LiNO_3$ per 100 grms. of soln*:

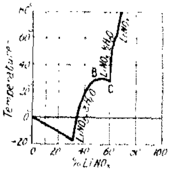

FIG. 82.—Solubility Curve of Lithium Nitrate

Temp. . . .	0·1°	19·05°	29·97°	29·64°	43·6°	60·0°	64·2°	70·9°
Solubility . .	34·8	40·4	56·42	57·48	60·08	63·6	64·9	66·1
Solid phase . .		*$LiNO_3.3H_2O$*			*$LiNO_3.\frac{1}{2}H_2O$*		*$LiNO_3$*	
Transition point .			← 29·6° →			← 61·1° →		

The cryohydric or eutectic temp. of the trihydrated salt is —17·8°, and the observed results are plotted in Fig. 82. The trihydrated salt melts at *B*, Fig. 82, the congruent m.p. 29·88°, at which temp. the crystalline trihydrated salt can be in equilibrium with two different sat. soln., one containing a larger and the other a smaller proportion of water than corresponds with $LiNO_3.3H_2O$. The transition point *C* of the trihydrated to the hemihydrated salt, 29·6°, is a little below the congruent m.p. of the trihydrated salt.

The solubilities of the other alkali nitrates in grams per 100 grms. of soln., are:

	0°	20°	40°	60°	80°	100°	120°
$NaNO_3$ . .	42·2	46·7	50·5	54·9	59·7	64·3	68·6
KNO_3 . .	11·7	24·0	39·0	52·0	62·8	71·1	83·1 (125°)
$RbNO_3$ . .	16·3	34·6	53·9	66·7	75·6	81·9	86·1 (118·3°)
$CsNO_3$ . .	8·54	18·7	32·1	45·6	57·3	66·3	68·8 (106·2°)

The terminal numbers with potassium, rubidium, and cæsium nitrates represent the b.p. of sat. soln. at nearly normal press.; for sodium nitrate the corresponding value is 67·6 (119°). Determinations of the solubility of sodium nitrate have been made by G. J. Mulder, Earl of Berkeley, A. Ditte, L. Maumené, A. Étard, etc.[30] The solubility curve of sodium nitrate has been carried upwards: 78·1 (180°), 83·5 (220°), 91·5 (225°), and 100 (313°), the last-named temp. represents the m.p. of the salt. According to L. C. de Coppet, the eutectic or cryohydric temp. of sodium nitrate is −18·5°, and the eutectic mixture is not a definite hydrate, $NaNO_3.7H_2O$, as A. Ditte once supposed. A. Étard represents the solubility *S*

at a temp. $\theta°$, between $-15°$ and $64°$, by $S=36 \cdot 0+0 \cdot 2784\theta$; and between $64°$ and $313°$, by $S=58 \cdot 0+0 \cdot 1686\theta$. The solubility data for potassium nitrate by G. J. Mulder, J. L. Andreae, A. Gerardin, A. Étard, H. Euler, H. Ost, A. Köhler, W. A. Tilden and W. A. Shenstone, Earl of Berkeley, L. Tschugaeff and W. Chlopin, etc., are available. For the solubility S of potassium nitrate at $\theta°$ between $-10°$ and $69°$, A. Étard gives $S=17 \cdot 0+0 \cdot 7118\theta$; between $69°$ and $125°$, $S=59 \cdot 0+0 \cdot 375\theta$; and between $125°$ and $338°$, $S=80+0 \cdot 0938\theta$. From $0°$ to $100°$, H. Kopp gives $S=13 \cdot 32+0 \cdot 5738\theta+0 \cdot 017168\theta^2+0 \cdot 0000035977\theta^3$; and A. E. Nordenskjöld—$\log S=0 \cdot 8755+0 \cdot 0020003\theta-0 \cdot 0000771 7\theta^2$. Other formulæ have been proposed by J. L. Andreae, etc. According to M. L. Frankenheim, the rhombohedral form of potassium nitrate is more soluble than the prismatic variety, and more readily forms under-cooled soln. The data for rubidium and cæsium nitrates are by the Earl of Berkeley. It will be observed that as in the case of the m.p. of the alkali nitrates the regular sequence is broken with rubidium nitrate, for its solubility is greater than that of potassium nitrate, while that of cæsium nitrate is less.

The general effect of salts with a like ion is to depress the solubility of a nitrate; this is the case with mixtures of potassium and sodium nitrates examined by T. Carnelley and A. Thomson, and W. W. J. Nicol;[31] with sodium nitrate and sodium hydroxide examined by R. Engel. J. N. Brönsted examined the effect of potassium hydroxide on the solubility of potassium nitrate. According to S. Tanatar, when an alkaline soln. of sodium nitrate is treated with hydrogen peroxide, and after evaporation at 50° until crystallization begins, treated with alcohol, crystals of a salt, **sodium peroxynitrate,** $NaNO_3.H_2O_2.8H_2O$, are formed. Potassium nitrate, carbonate, and hydrocarbonate were examined by C. Touren; sodium, potassium, and ammonium nitrates by A. Winkelmann,[32] F. Rüdorff, and C. J. B. Karsten. Mixed crystals are formed with potassium nitrate and silver or thallium nitrate, and the solubility of the alkali nitrate increases with increasing proportions of the other salts.[33] A. Étard[34] has studied the effect of sodium chloride on the solubility of potassium nitrate in water. W. Meyerhoffer[35] has studied the reversible reaction between sodium or potassium nitrate and ammonium chloride; and F. Rüdorff with potassium nitrate and ammonium sulphate.

Analyses of the mineral *darapskite*, by A. Dietze,[36] agree with $Na_2SO_4.NaNO_3.H_2O$, **hydrated sodium nitratosulphate.** It occurs in the Pampa del Toro (Atacama, Chili) in monoclinic prisms with axial ratios $a:b:c=1 \cdot 5258:1:0 \cdot 7514$; $\beta=102° 55'$; and sp. gr. 2·203. J. C. G. de Marignac made artificial crystals of sp. gr. 21·97 by evaporating mixed soln. of the two salts; he thought his crystals had $1\frac{1}{2}H_2O$, but A. von Schulten showed that they are identical with darapskite. The composition of the so-called *nitroglauberite* corresponds with a **trihydrated sodium trinitrato-sulphate,** $2Na_2SO_4.6NaNO_3.3H_2O$, but whether it is a mixture or true chemical individual is not clear. It is found in the nitre deposits of Villanueva, Atacama. Analyses of some samples have half the above quantity of water.[37] Artificial crystals have been made. A. Massink studied the ternary system $K_2SO_4-KNO_3-H_2O$ at 35°; the ternary system $Li_2SO_4-LiNO_3-H_2O$ at 25° and 35°; and Na_2SO_4—$NaNO_3$—H_2O at 10°, 20°, 25°, 30°, 34°, and 35°. He found the double salts **lithium nitrato-sulphate,** $9Li_2SO_4.LiNO_3.27H_2O$ and $11Li_2SO_4.LiNO_3.17H_2O$, exist at 35° but not at 25°; **sodium nitrato-sulphate,** $NaNO_3.Na_2SO_4.H_2O$, does not exist below 12·8°; $3NaNO_3.4Na_2SO_4$ is stable between 20° and 35°; and $3NaNO_3.2Na_2SO_4$, between 30° and 35°.

Sodium and potassium nitrates are soluble in liquid *ammonia*,[38] and the soln. are good electrical conductors. According to F. M. Raoult, the dry salts absorb no ammonia, but a conc. soln. of sodium nitrate dissolves as much ammonia as an equal volume of water, and a conc. soln. of potassium nitrate, more ammonia than water. R. Abegg and H. Riesenfeld found the tension of $\frac{1}{2}N$-, N-, and $1 \cdot 5N$-soln. of potassium nitrate in N-soln. of ammonia at 25°, had vap. press. 14·59, 15·61, and 16·75 mm. respectively, when the N-ammonia alone had a vap. press. of 13·45 mm. F. Ephraim prepared *lithium tetrammino-nitrate*, $LiNO_3.4NH_3$, as a syrup more stable than the corresponding tetrammino-chloride. The electrical conductivities and the lowering of the f.p. of soln. of potassium nitrate[39] in soln.

of liquid *hydrogen cyanide*, show that the salt is ionized even more than in water, a fact thought to be explained by the high dielectric constant of the solvent. According to C. G. Gmelin,[40] lithium nitrate is soluble in conc. *ethyl alcohol*; solubility data for sodium nitrate in ethyl alcohol have been given by J. J. Pohl, G. C. Wittstein, A. E. Taylor, H. A. Bathrick, and G. Bodländer; and for potassium nitrate by A. Gérardin, G. Bodländer, and H. A. Bathrick. The results can be represented by a general formula of the type $(x+a)(y+b)^n$=constant, or $(x+a)y$=constant, where a, b, and n are constants, n is independent of the temp., and a and b vary with temp.; x represents the solubility of the salt, and y the amount of alcohol (or acetone) in grms. per 100 grms. of water. According to C. A. L. de Bruyn, 100 grms. of absolute *methyl alcohol* at 25° dissolve 0·41 grm. of sodium nitrate, and 100 grms. of ethyl alcohol at 25° dissolve 0·036 grm. of the same salt. According to A. E. Taylor, at 30°, for alcohol of different percentage amounts p of C_2H_5OH, 100 grms. of soln. dissolve in w grms. of $NaNO_3$ at 30°: p=5, w=46·41; p=10, w=43·50; p=30, w=31·31; p=50, w=18·94; p=70, w=7·81; p=90, w=1·21. Similarly, for potassium nitrate, for 100 grms. of aq. alcohol with p per cent. of C_2H_5OH at 30°: p=8·25, w=32·3; p=17, w=22·4; p=44·9, w=7·0; p=65, w=2·7; p=88, w=0·4. A. Gérardin also showed that the *solubility in alcohol rises with temp. from 17 grms. of salt per 100 grms. of 5·5* per cent. alcohol at 10° to 93 grms. of salt at 60°; and with 90 per cent. alcohol, gram 0·2 at 10° to 1·1 at 60°. The ternary systems alcohol—water—salt have been studied by G. Bodländer, A. E. Taylor, and H. A. Bathrick. According to A. Schlamp, potassium nitrate is insoluble in propyl alcohol. The solubility of sodium or potassium nitrate in aq. *acetone* has been studied by A. E. Taylor, and H. A. Bathrick. 100 grms. of a 16·8 per cent. soln. of acetone dissolve 78·3 grms. of sodium nitrate, and 38·9 grms. of potassium nitrate; similarly, 44·1 per cent. acetone dissolves 46·2 grms. of sodium nitrate, and 17·0 grms. of potassium nitrate; and 87·6 per cent. acetone, 3·2 grms. of sodium nitrate, and 0·7 grm. of potassium nitrate. According to A. Köhler, 100 grms. of a sat. soln. contain 61·36 grms. of *sugar* and 11·45 grms. of potassium nitrate, at 31·25°. According to A. Vogel, 100 parts of *glycerol*, sp. gr. 1·225, dissolve 10 parts of potassium nitrate.

The **specific gravities of aqueous solutions** of lithium nitrate at 19·5°, by P. Kremers[41] are 1·069 for a soln. of 12·7 grms. of the salt per 100 grms. of water, and 1·197 for 41·8 grms., 1·319 for 79·4 grms. P. Kremers, H. Schiff, and others have measured the sp. gr. of soln. of sodium nitrate. H. Schiff gives at 20·2°:

Per cent. $NaNO_3$	5	10	15	20	30	40	50
Sp. gr.	1·033	1·068	1·103	1·142	1·224	1·315	1·418

G. T. Gerlach gives for soln. of potassium nitrate at 15°:

Per cent. KNO_3	1	2	5	10	15	20	21
Sp. gr.	1·00641	1·61283	1·03207	1·06524	1·09977	1·13599	1·14361

F. L. Haigh gives for the sp. gr. of N- and $\frac{1}{2}N$-soln. of the alkali nitrates, at 20°/4°:

	$LiNO_3$	NH_4NO_3	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$
N-soln.	1·03803	1·03043	1·05386	1·05954	1·10083	1·14091
$\frac{1}{2}N$-soln.	1·01830	1·01450	1·02646	1·02932	1·04989	1·07001

S. Lussana found that the temp. θ of maximum density of 0·65 and 1·30 per cent. soln. of potassium nitrate is related with the press. p respectively by $\theta=2·89-0·0133(p-1)$, and $\theta=1·84-0·0124(p-1)$. The lowering of the **vapour pressure** of aq. soln. of lithium nitrate at different temp. has been measured by G. Tammann, and by A. T. Lincoln and D. Klein[42] at 25°, and the results show that the relative lowering of the vap. press. with increasing conc. increases in accord with the assumption that the salt forms hydrates in aq. soln. The vap. press. of aq. soln. of sodium nitrate have been measured by C. Dieterici, A. Smits, W. W. J. Nicol, G. Tammann, and by A. T. Lincoln and D. Klein. According to

A. Speransky, the vap. press. p of a sat. soln. of sodium nitrate at T° K. can be represented by Bertrand's formula $\log p=7.5172+50 \log [(T-74.8)/T]$. The mol. wt. calculated from the lowering of the vap. press. corresponds with a very large percentage ionization, and the decrease which occurs with an increasing conc. shows that there is a disturbing factor—hydration. Similar remarks apply to the results with potassium nitrate soln. G. Tammann has studied the lowering of the vap. press. of water, at 100°, by soln. of the alkali nitrates. E. B. R. Prideaux studied the vap. press. of soln. of sodium and potassium nitrates, and studied the deliquescence and drying of these salts.

Anhydrous lithium nitrate is very deliquescent; and sodium nitrate is also deliquescent. Since the last-named salt becomes damp on exposure to the air it cannot be used for some purposes for which potassium nitrate is applicable. Potassium, rubidium, and cæsium nitrates do not deliquesce under the same conditions, although G. J. Mulder[43] showed that if potassium nitrate be confined under a bell-jar over water at 14° to 20°, it does deliquesce; and F. L. Kortright found the same salt at 20° to deliquesce when the partial press. of the water vapour exceeds 15·5–16·5 mm., and sodium nitrate when the partial press. of the water vapour exceeds 12·3–13·5 mm. A salt can be deliquescent only when the press. of the water vapour from its sat. soln. exceeds the partial press. of the water vapour in the surrounding air. If p_1 be the vap. press. of water, p, the vap. press. of a sat. soln. of the salt containing S grms. of salt per 100 grms. of water, and k be the constant of proportion to be evaluated from the observed data, R. Emden has shown that $Sk=(p-p_1)/p$, which enables p_1 to be computed from the values of p and S. The deliquescence press. of the water vapour for sodium nitrate at 0°, 10°, 20°, and 30° is then 3·5, 6·9, 12·8, and 22·6 mm. respectively, and for potassium nitrate, 4·4, 8·7, 16·0, and 28·3 mm. respectively.

The **boiling point** of a sat. soln.[44] of lithium nitrate is 200°; sodium nitrate, 120·2°; and potassium nitrate, 115·549°. A. Smits found a second b.p. with sat. soln. of sodium nitrate at 310°, and with potassium nitrate at 311°. The m.p. may be regarded as a terminal point on the solubility curve, and since the curve showing the vap. press. of sat. soln. usually rises with temp., it follows that since the non-volatile salt has no vap. press. at its m.p., there must be a maximum in the vap. press. curve. If this maximum be greater than the atm. press., so must the sat. soln. have two b.p. A. Smits[45] has studied the b.p. of soln. of sodium nitrate and found the mol. lowering decreases from 0·95° with soln. containing 0·0462 mol. per litre to 0·89° with soln. containing 0·863 mol. per litre. Similarly, with soln. containing 0·0499 and 6·993 mols. of potassium nitrate per litre, the mol. lowering of the b.p. falls from 1·0° to 0·669°.

The **freezing points** of aq. soln. of lithium nitrate show that in dil. soln. the solute is largely ionized, but that in conc. soln., the mol. lowering of the f.p. is greater than corresponds with complete ionization, and this is explained, as in analogous cases, by assuming that the ions of the solute are hydrated. Similar remarks apply to the mol. lowering of the f.p. which falls from 3·6° to 3·15° in passing from soln. with 0·0100 to soln. with 1·000 mol. per litre. Likewise with potassium nitrate, there is a drop from 3·5° to 2·66° in passing from soln. with 0·0100 to soln. with 1·000 mol. per litre. According to W. Biltz,[46] with rubidium nitrate the mol. lowering of the f.p. falls from 3·6° to 2·64° in passing from soln. with a conc. of 0·0393 to those with a conc. of 0·8293 mol. per litre. The corresponding degrees of ionization are $\alpha=0.941$ and 0.429 respectively; and W. Ostwald's constant $K=\alpha^2/(1-\alpha)v$ simultaneously falls from 0·47 to 0·27, as also occurs with other strong electrolytes; on the contrary, W. Biltz found that soln. of cæsium nitrate behaved more like weak electrolytes in that the depressions of the f.p. are 0·028°, 0·460°, and 1·267° with soln. containing respectively 0·00766, 0·1421, and 0·4339 mol. per litre. The corresponding degrees of ionization are respectively $\alpha=0.98$, 0·75, and 0·578; and the values of Ostwald's constant, 0·33, 0·32, and 0·34 respectively. Lithium and sodium nitrates have a strong negative **double**

refraction, that of potassium nitrate is weaker, while rubidium and cæsium nitrates have a feeble positive double refraction.[47] The **refractive indices** of sodium nitrate for the ordinary ω and extraordinary ϵ rays are :

		B-line	*D*-line	*E*-line	*H*-line
$NaNO_3$	ω	1·5793	1·5863	1·5954	1·6260
	ϵ	1·3346	1·3358	1·3374	1·3440
KNO_3	α	1·3328	1·3346	1·3365	1·3436
	β	1·4988	1·5056	1·5124	1·5385
	γ	1·4994	1·5064	1·5135	1·5405

The index of refraction of soln. of the alkali nitrates at 20° for sodium light is :

	$LiNO_3$	NH_4NO_3	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$
N-soln.	1·34123	1·34251	1·34174	1·34182	1·34268	1·34492
½*N*-soln.	1·33648	1·33776	1·33751	1·33743	1·33785	1·33902

For rubidium nitrate the refractive indices for the *D*-line in the direction α is approximately 1·51 ; β, 1·52 ; γ, 1·524. J. H. Gladstone and W. Hibbert[48] give for the mol. refraction for the *D*-line of a 5·12 per cent. soln. of lithium nitrate, 17·72 ; and for a 42·18 per cent. soln., 17·91 ; for a 44·35 per cent. soln. of sodium nitrate, 18·53 ; and for a 4·76 per cent. soln. of potassium nitrate, 22·24 ; and for a 17·55 per cent. soln., 22·26. The **magnetic rotations**[49] of 18·17, 26·16, and 56·56 per cent. soln. of lithium nitrate are respectively 0·9637, 0·9477, and 0·8661, or the mol. rotations are 18·195, 11·799, and 4·068 respectively. The alkali nitrates are diamagnetic.[50] L. Arons gives the **dielectric constant** of potassium nitrate as 2·56.

In 1801, H. Davy stated that fused potassium nitrate conducts electricity. M. Faraday also made observations on this subject. The **electrical conductivity** of solid sodium nitrate at 52° is $0·662\times10^{-12}$ reciprocal ohms ; at 200°, $0·176\times10^{-7}$; and at 289°, $0·155\times10^{-4}$; for the molten salt at 300°, 0·441 ; and at 356°, 0·666 reciprocal ohms. R. Foussereau[51] also found for solid potassium nitrate, a conductivity of $0·312\times10^{-12}$ at 30° ; $0·568\times10^{-10}$ at 100° ; $0·106\times10^{-6}$ at 200° ; and $0·340\times10^{-4}$ reciprocal ohms at 300°. For the molten salt at 355°, R. Foussereau also found 0·7656 reciprocal ohm at 355°, and L. Graetz, 0·8631 at 380°. F. M. Jäger and B. Kampa measured the molecular conductivity, μ, of lithium nitrate at elevated temp. and found for temp. between 272 and 487·3°, $\mu=41·14-0·238(\theta-300)$; for sodium nitrate between 321·5° and 487·3°, $\mu=41·56+0·205(\theta-300)$; for potassium nitrate between 346·1° and 500·4°, $\mu=36·21+0·1875(\theta-350)$; for rubidium nitrate between 318·8° and 493°, $\mu=33·51+0·145(\theta-300)$; and for cæsium nitrate between 446·6° and 556·3°, $\mu=42·13+0·120(\theta-300)$. C. Sandonnini measured the conductivity of fused mixtures of potassium and sodium nitrates. P. Walden studied the relation between the conductivity and viscosity of aq. soln. of lithium nitrate, etc. The eq. electrical conductivities, λ, of soln.[52] containing a mol. of the nitrate in v litres of water at 25°, are :

v	32	64	128	256	512	1024
$LiNO_3$	97·9	100·7	104·1	106·6	108·2	108·7
$NaNO_3$	108·2	111·8	114·7	117·5	119·4	120·1
KNO_3	128·0	132·4	136·4	139·5	141·7	141·8
$RbNO_3$	131·6	134·4	137·25	141·1	142·3	143·5
$CsNO_3$	134·2	138·2	139·3	141·9	144·7	146·4

Unlike the results calculated for degrees of ionization from the depressions of the f.p., the values of Ostwald's constant computed from the electric conductivities of soln. of rubidium nitrate show marked deviations from constancy and they are thus constant with results with other strong electrolytes—the rubidium ion $Rb^{\cdot}$ and the NO'_3-ion are among those with the greatest electro-affinities. The electrical conductivity of lithium nitrate is greater in methyl alcohol than in water, but in

mixtures of methyl or ethyl alcohol and water there is a minimum in the electrical conductivity corresponding not with a minimum value in the degree of ionization, but with a maximum value in the viscosity of the solvent. The decomposition potential of normal lithium nitrate soln. is 2·11 volt. O. Gropp measured the effect of temp. on the conductivity of liquid and frozen soln. of sodium nitrate. The temp. coeff.[53] of 0·01N-soln. of sodium nitrate is 0·0226 between 18° and 26°, and for potassium nitrate between 18° and 52°, 0·0223. E. Horngacker studied the products of the electrolysis of soln. of potassium nitrate by alternating and continuous currents; and W. Chauffal, likewise, of soln. of sodium nitrate. The **transport numbers**[54] of the anion, NO'_3, in 0·5N- and 4N-soln. of sodium nitrate are respectively 0·629 (19°) and 0·600 (9°); and with 0·1N-soln. of potassium nitrate 0·497 and 0·487 respectively. G. Carrara has measured the transport number for lithium nitrate ions. A. Heydweiller gave respectively 2·72 and 4·99 for the **dielectric constant** of powdered and compact potassium nitrate; L. Arons found 2·18 for sodium nitrate, and 2·56 for potassium nitrate.

According to J. S. Stas,[55] a soln. of lithium or potassium nitrate which has been melted, blues red litmus. According to J. Scobai, potassium nitrate is not decomposed at 410°. When heated to redness, the alkali nitrates first give off oxygen, forming the alkali nitrite, MNO_2, for example, $2KNO_3=2KNO_2+O_2$; then a mixture of oxygen and nitrogen is given off and a mixture of the alkali oxide and peroxide is formed. If the operation is conducted in earthen or glass vessels, some alkali silicate is formed; metal vessels are also attacked—silver and gold less than platinum.[56] Under press., the decomposition is hindered; thus, C. J. B. Karsten claims to have heated potassium nitrate for 15 minutes to a red heat in a copper vessel without decomposition. According to F. Reich and H. Rose, the nitrate is decomposed when fused with siliceous materials, forming an alkali silicate. When dried and powdered nitre is thrown on red-hot charcoal or when powdered charcoal is sprinkled on fused nitre, rapid combustion occurs, possibly: $4KNO_3+5C=2K_2CO_3+3CO_2+2N_2$, so that one volume of solid nitre will give nearly 3000 times its bulk of gas, and it is this fact which renders nitre available for use in the manufacture of *gunpowder*—a mixture of carbon, sulphur, and nitre. According to A. Cavazzi,[57] a mixture of nitre with sodium thiosulphate, $Na_2S_2O_3$, is also explosive, so also is a mixture of sodium hypophosphite, NaH_2PO_2, and nitre a powerful detonator: $NaH_2PO_2+2NaNO_3=Na_3PO_4+H_2O+NO_2+NO$. H. Rose says powdered potassium nitrate copiously absorbs the vapours of anhydrous sulphuric acid, H_2SO_4, to form a pasty mass; and, according to C. Schultz-Sellack, potassium nitrate unites with liquid sulphur dioxide, forming a mixture or compound of the alkali nitrite and sulphate.

According to E. Laurent,[58] a soln. of sodium nitrate is decomposed in sunlight with the evolution of oxygen, while in darkness it is stable. Zinc dust reduces a soln. of potassium nitrate to the nitrite and hydroxide with the evolution of some oxygen; above 60°, only a little nitrite but much nitrogen and ammonia are given off.[59] The copper-zinc couple also reduces soln. of the nitrate, first to nitrite, and then to ammonia. Potassium amalgam, stannous chloride, etc., also reduce the nitrates in a similar way.

According to C. Schultz,[60] 100 grms. of nitric acid, $HNO_3.H_2O$, dissolve 0·5 grm. of lithium nitrate; 1·5 grms. of sodium nitrate; or 71 grms. of potassium nitrate; rubidium and cæsium nitrates also dissolve readily in the acid. According to R. Engel, when nitric acid is added to a sat. soln. of potassium nitrate, at 0°, each mol. of HNO_3 precipitates a mol. of the salt until about 30 mols. have been displaced, when the solubility of the salt in the acid increases, probably owing to the formation of acid nitrates. Expressing the conc. of the nitric acid, HNO_3, and potassium nitrate in grams per 100 grms. of soln., R. Engel found at 0°:

HNO_3	0	3·71	8·38	13·58	19·47	30·04	42·86	75·95
KNO_3	12·65	10·02	8·38	7·49	7·49	7·68	10·42	28·64

The increased solubility of the potassium nitrate when the conc. of the acid exceeds about 19·47 per cent. is attributed to the formation of acid or hydro-nitrates.

Definite acid nitrates of potassium, rubidium, and cæsium have been isolated by H. L. Wells and F. J. Metzger, and E. Groschuff. The solubility curve of potassium nitrate expressed in mol. of salt per 100 mols. of the soln. of nitric acid of sp. gr. 1·5, is indicated in Fig. 83. **Potassium dihydro-nitrate,** $KNO_3.2HNO_3$, was prepared by E. Groschuff, by dissolving 101·6 grms. of potassium nitrate in 126·1 grms. of nitric acid, sp. gr. 1·5, and cooling the soln. by a freezing mixture. Prismatic crystals, melting at 22°, separated out. The dihydro-nitrate and the normal nitrate form a eutectic, melting at 21°. This salt was made by A. Ditte in 1879, and by H. L. Wells and F. J. Metzger in 1901. **Potassium hydro-nitrate,** $KNO_3.HNO_3$, is difficult to make, since it readily forms supersaturated soln., and is very hygroscopic; it is decomposed by water. It is obtained in crystalline plates by keeping a supersaturated soln. between 22° and 28° for some time. It is also made by freezing a soln. in a mixture of carbon dioxide and ether, and warming the mass as rapidly as possible to 23°, and holding it there some time. Between 28° and 29° the hydro-nitrate decomposes into the neutral salt and acid soln.; while the hydro-nitrate is decomposed by water, the dihydro-nitrate dissolves in water without decomposition. The soln. of these two compounds, as well as others, is an interesting illustration of the fact that monobasic acids—like nitric and hydrochloric acids—can form acid salts, and that hydrofluoric acid does not necessarily owe its remarkable tendency to form acid salts to its being dibasic, H_2F_2.

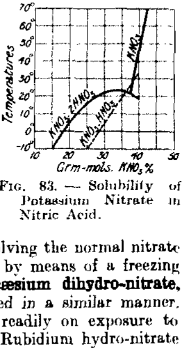

FIG. 83. — Solubility of Potassium Nitrate in Nitric Acid.

The monoacid nitrate—**rubidium hydro-nitrate,** $RbNO_3.HNO_3$—is prepared in small octohedral crystals melting at 62°, by saturating nitric acid of sp. gr. 1·42 with the normal nitrate at a gentle heat, and cooling by means of a freezing mixture. Small octohedral crystals of the corresponding **cæsium hydro-nitrate,** $CsNO_3.HNO_3$, are obtained in a similar manner, but a freezing mixture is not necessary. The crystals melt at 100°. Potassium dihydro-nitrate, $KNO_3.2HNO_3$, and likewise rubidium diacid nitrate, or **rubidium dihydro-nitrate,** $RbNO_3.2HNO_3$, are obtained, in colourless transparent needle-like crystals, melting between 39° and 46°, by dissolving the normal nitrate to saturation in nitric acid of sp. gr. 1·50, and cooling, by means of a freezing mixture, below 0°. Colourless transparent plates of **cæsium dihydro-nitrate,** $CsNO_3.2HNO_3$, melting between 32° and 36°, are obtained in a similar manner. All the acid nitrates give off nitric acid more or less readily on exposure to air, and rubidium dihydro-nitrate decomposes rapidly. Rubidium hydro-nitrate and the two cæsium salts are more stable. The monoacid salts can be preserved indefinitely in sealed tubes. The acid nitrate, $RbNO_3.2\frac{1}{2}HNO_3$, reported by A. Ditte, is probably the impure diacid salt. A. Ditte's conclusion is based on an analysis of the *solution* obtained by saturating nitric acid, HNO_3, with rubidium nitrate.

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§ 37. Gunpowder

Of the mischievous composition and diabolical abuse of gunpowder much might he written; but because the present world taketh delight only in shedding innocent blood, and cannot endure that unrighteous things should be reproved, and good things praised, therefore it is best to be silent.—J. R. GLAUBER (1658).

If potassium nitrate be mixed with powdered charcoal, and heated, the two materials react with explosive violence, forming potassium carbonate, nitrogen, and carbon dioxide: $4KNO_3+5C=2K_2CO_3+2N_2+3CO_2$. The volume of the gases produced is so much greater than that of the original volume of the mixed solids that if the powder be ignited in a closed space, the expanding gases give the

mixture its characteristic propelling, tearing, and splitting powers. It was soon found that the explosive effect was augmented if the nitre and charcoal be mixed with sulphur, so that instead of a residue of solid potassium carbonate a mixture of solid potassium sulphide, sulphate, and carbonate was obtained. The mixture is called gunpowder. The action of the sulphur is: (i) To lower the temp. of ignition of the powder; since sulphur inflames near 250°, and by its combustion raises the temp. to the fusion point of saltpetre, 335°. This latter temp. would be near the ignition point of the powder without sulphur. (ii) The sulphur also increases the speed of the combustion.

According to the old theory of the reaction: $4KNO_3+2S+6C=2K_2S+2N_2+6CO_2$, it follows that the theoretical mixture will contain 404 grms. of potassium nitrate; 64 grms. of sulphur; and 72 grms. of carbon. Otherwise expressed, 75 per cent. of nitre; 12 per cent. of sulphur; and 13 per cent. of charcoal. This very nearly represents the average composition of gunpowder for the standard mixture for dried service gunpowder is: nitre, 75; charcoal, 15; sulphur, 10—in many sporting powders, the proportion of nitre is rather greater than this. With *military powder* great propulsive force is required; with *sporting powder*, quick ignition and combustion; and with *blasting powder*, a large volume of gas at a high temp. The effectiveness and utility of black powder depends not only on its composition, but also on the intimacy of the admixture of the various components, the density and uniformity of the grams, and the grain-size of the particles. The following will give some idea how gunpowder is manufactured:

The three ingredients are first (1) purified, if necessary; and then (2) ground to powder. The nitre and sulphur are pulverized together in rotating iron or wooden drums containing bronze balls; and then (3) intimately mixed with the desired proportions of charcoal previously pulverized. The mixing is effected in rotating drums of thick leather containing hard-wood balls Various other modes of mixing and pulverizing are also used. The loose powder so obtained—the green charge—is not used for gunpowder, but it can be used in the manufacture of fireworks. (4) The powder is then moistened with 10–20 per cent. of water, and milled in an incorporating mill for a few hours. (5) The mass is then passed through a pair of fluted bronze rollers when it forms the so-called *mill-cake*. (6) The latter is passed through plain rollers so as to break it into what is called *meal*. (7) The meal is pressed into cakes under high press.—*press-cake*—and the product is now gunpowder. (8) The press-cake is then granulated by pressing it through successive sets of gun-metal or bronze fluted rollers, whence it passes through vibrating sieves, where the grains are sorted into various grades of approximately uniform size. (9) The gunpowder is then slowly rotated in wooden drums, when mere friction imparts to the surface of the grains a fine glaze or polish, and at the same time the sharp corners of the grains are rounded off, and the pores closed up. With the coarse-grained powders, a little graphite may be added to the charge in the glazing drum. (10) The polished powder is dried, and "finished" in a second rotation in a polishing machine. (11) The "finished" powder is blended by mixing together different proportions of different batches so as to give as uniform a quality of gunpowder as possible.

A. V. P. d'Antonj noticed,[1] in 1765, that the more rarefied the atm. in which the powder burns, the more difficult is the ignition, and that the powder melts when heated in vacuo. Similar results were obtained by G. W. Muncke (1817). J. N. Hearder (1865) electrically heated a platinum wire in contact with gunpowder in vacuo, no explosion occurred, the nitre melted, and sulphur sublimed; but B. U. Bianchi (1862) found that under similar conditions the powder burned slowly without deflagration; and M. Heeren (1886), and F. A. Abel (1869), showed that under a press. of 150–510 mm. the grains in the immediate vicinity of the walls of the vessel melted and sulphur sublimed; and, as indicated by B. U. Bianchi, after a time the grains ignited and scattered the un-ignited powder about the exhausted vessel. At a press. of 760 mm. the powder inflamed in a few seconds. F. Hauksbee (1702) found a cubic centimetre of black gunpowder gave 232 c.c. of gas reduced to standard conditions; B. Robins (1742) found 244 c.c.; and C. J. Brianchon (1822), 400 c.c. J. L. Gay Lussac and M. E. Chevreul are said to have first analyzed the gases and solid residue formed during the combustion of

gunpowder. J. L. Gay Lussac obtained 449·5 litres of gas from 900 grms. or one litre of powder. The gas contained approximately :

CO_2	N_2	CO	NO	CH_n	CH_mO_n
44·3	35·7	4·8	7·7	0·6	7·9 per cent.

The solid residue contained potassium sulphate, carbonate, sulphide, and polysulphides.

R. Bunsen and L. Schischkoff,[2] and J. Linck examined the products of combustion under relative low press. ; and L. von Károlyi, A. Vignotti, N. Federoff, and B. F. Craig under high press. The results show that the products of combustion differ when the explosion is produced under a low and under a high press. such as must occur when gunpowder is employed as an explosive. Under low press., for example, potassium sulphate remains, but under high press. the sulphate is reduced to sulphide. A. Noble and F. A. Abel (1874-1880), and H Debus (1882) made extensive experiments on the combustion of black powder. The results with pebble powder, P, and blasting powder, B, under press. are as follows :

Gaseous products (mean)—P . . 44·01 ; and B . . 51·35 per cent.

	CO_2	CO	N_2	H_2S	C_2H_4	H_2
P	26·45	4·69	11·39	1·27	0·07	0·06
B	22·79	15·22	8·58	3·89	0·70	0·17

Solid products (mean)—P . . 55·97 ; and B . . 48·65 per cent.

	K_2CO_3	K_2SO_4	K_2S_2	KCyS	KNO_3	NH_4CO_3	S	C
P	33·44	6·93	9·57	0·18	0·13	0·06	4·20	—
B	19·45	0·28	17·45	1·38	0·04	0·84	6·64	0·95

In some cases free oxygen was observed as was first noted by R. Bunsen and L. Schischkoff. Fine-grained powders give a smaller proportion of gaseous products than coarse-grained powders ; and the coarse-grained powders less than pellet powders.

According to H. Debus, the combustion of the powder takes place in two consecutive stages : (1) An oxidizing reaction which occupies a very short space of time, and which constitutes the explosion. Here potassium sulphate and carbonate, carbon dioxide, nitrogen, and possibly also carbon monoxide, are formed—say : $16KNO_3+13C+5S=3K_2CO_3+5K_2SO_4+9CO_2+4CO+8N_2$, *some sulphur and carbon* are not acted upon. (2) A reducing reaction which occurs while the products of *the first stage are under great press. and at a very high temp. and in which some* potassium sulphate is reduced by carbon : $4K_2SO_4+7C=2K_2CO_3+2K_2S_2+5CO_2$, and potassium carbonate by sulphur : $4K_2CO_3+7S=K_2SO_4+3K_2S_2+4CO_2$. A little sulphur unites with the metal of the gun, and a little with the hydrogen and moisture occluded by the charcoal. Making a small allowance for this, the combustion of service gunpowder can be represented : $16KNO_3+21C+5S=5K_2CO_3+K_2SO_4+2K_2S_2+13CO_2+3CO+8N_2$. A gram of powder, therefore, gives 264·6 c.c. of gas at n.p.t. A. Noble and F. A. Abel found 263·74 c.c. They also found the heat of combustion to be 714·5 Cals. per gram of powder. They also add : " The decomposition which an average gunpowder undergoes when fired in a closed space cannot be represented by even a comparatively complicated chemical equation."

The potential energy of an explosive depends on : (1) The volume of gas generated—calculated for purposes of comparison purposes at 760 mm. and 0° ; and (2) on the temp. developed on explosion, whereby the gases are expanded enormously. A. Noble and F. Abel estimate the total work theoretically performable is 332,000 gram-metres per gram, or 486 foot-tons per lb. of powder.

To calculate the approximate pressure developed during the explosion of gunpowder in a closed vessel.—According to the old theoretical equation : $4KNO_3+2S+6C=2K_2S+2N_2+6CO_2$, gunpowder on explosion furnishes 59 per cent. of gas ; or one grm. of gunpowder, at 0°, and 760 mm. press., furnishes 247·3 c.c. of carbon dioxide and 79 c.c. of nitrogen ; in all, 327 c.c. of gas consisting of 0·49 grm. of carbon dioxide ; 0·10 grm. of nitrogen ;

and 0·41 grm. of potassium sulphide. Again, one grm. of an average gunpowder occupies 0·9 c.c. The surface exposed by one c.c. is 6 square cm., hence, 0·9 c.c. will expose 5·4 square cm. But if 0·9 c.c. of gunpowder be confined at atm. press., it follows that 327 c.c. will be confined under 327÷0·9=363·2 atm. press.; or, if one gram of gunpowder at 0° be confined in a closed space and exploded, it furnishes sufficient gas to give 363·2÷5·4=67·3 atm. press. per square cm. supposing the temp. were constant—but the temp. does not remain constant.

To calculate the approximate temperature developed during the explosion of gunpowder in a closed vessel.—The reaction indicated above is exothermal, and much heat is developed. The rise of temp. will cause the gas to expand with an ever-increasing press. One gram of carbon in burning to carbon dioxide develops 8080 cals. Hence, 0·13 grm. of carbon will furnish 1050 cals. Assuming that the sp. ht.—that is, the amount of heat required to raise the temp. of one gram of the substance 1°—is constant; and that the sp. ht. of carbon dioxide is 0·22; of potassium sulphide, 0·4; and of nitrogen, 0·24; remembering also that the quantity of heat Q is equal to the product of the weight of the substance heated, w, the rise of temp., x, and the sp. ht., s, we have $Q=wsx$; or, as a first approximation, $1050=\{(0\cdot49\times0\cdot22)+(0\cdot1\times0\cdot24)+(0\cdot41\times0\cdot4)\}x$; or, $x=3540°$. This means that the combustion of one gram of gunpowder will give sufficient heat to raise the temp. of the products of combustion 3540°—F. Abel and A. Noble's value 3200°.

If 326 c.c. of gas be heated to 3540°, the press. corresponds with 880 atm. per square cm. Experiment shows that the observed press. is but half that indicated by this theoretical discussion. The difference is due to several disturbing effects. (1) The analysis of the gaseous products of combustion shows that side reactions must also be in progress, for part of the oxygen forms K_2SO_4, some of the carbon burns to carbon monoxide; some of the nitrogen to nitric oxide; some hydrogen and hydrogen sulphide are produced by the decomposition of the water present in gunpowder; and some of the gunpowder remains unburnt; (2) the apparatus in which the test is made is slightly elastic, and this interferes with the accurate measurements of the press.; (3) the sp. ht. of the gas increases appreciably with rise of temp.; and (4) the containing vessel itself absorbs some heat, and this the more, the slower the explosion.

When used as a propellant in a big gun, combustion should commence slowly, so as to gradually overcome the *vis inertiæ* of the projectile; and, as the projectile travels towards the muzzle of the gun, the speed of combustion should increase rapidly, so that the projectile has acquired its maximum velocity as it reaches the muzzle of the gun. The rate of combustion of the power is more easily controlled by varying the size and shape of the grains; by varying the density of the powder; and by varying the surface coating of the individual grains. For very big guns, requiring a big charge, the burning of the gunpowder even in rounded pellets or cubical pebbles one and a half inches in diameter, is too violent at the beginning. The difficulty was to some extent overcome [3] by using charges built up with perforated slabs so as to expose a minimum surface of powder at the beginning of the combustion, and later, the slabs with larger and larger holes produced a greater and greater surface of powder, and a more and more rapid combustion. In accordance with this idea, the so-called *prism powder* was made in which the rapidity of combustion is progressively increased from the start by moulding the powder into a prism with a hollow core, so that combustion, from within towards the outer surface, increases in velocity as the surface grows larger, until at last the prism breaks up, converting it at the last instant into what is practically a coarse-grained powder.

In order to secure still slower combustion with low initial strain and a longer sustained action, so as to reduce the strain on the breech of the gun, with heavy ordnance, charcoal charred at a low temp. is used; this enables the powder to retain a certain percentage of moisture, and in *brown gunpowder* or *cocoa powder*—so named on account of its colour—the proportion of nitre is higher and that of the sulphur lower than in ordinary gunpowder; semi-charred wood-fibre, or straw carbonized by superheated steam, is used as the source of charcoal. The composition of brown gunpowder is approximately: nitre, 79; charcoal, 18; sulphur, 3. According to A. Noble, the combustion of cocoa powder under press. gives per kilogram, 195 litres of gas, and 837 Cals. of heat. The gas has the composition:

CO_2	CO	H_2	CH_4	N_2
51·30	3·42	3·26	0·31	41·71 per cent.

There is no potassium sulphide in the solid residue, but 64·12 per cent. of K_2CO_3; 13·55 per cent. of $KHCO_3$; and 22·33 per cent. of K_2SO_4. The larger volume of water vapour present in cocoa powder makes the volume of gas at the moment of explosion nearly the same as with ordinary black powder. Thus a kilogram of black powder gives 263·7 litres of permanent gas and 40·9 litres of water vapour, while a kilogram of cocoa powder gives 195·4 litres of permanent gas and 122·5 litres of water vapour. If cocoa powder be exploded under atm. press., large quantities of nitre remain undecomposed.

There is another series of explosives which do their work by forming large volumes of gas during their decomposition. *Nitro-glycerol*, for instance, is made by nitrating glycerol with conc. nitric acid; *tri-nitrotoluene* is made similarly from toluene; and *gun cotton*, or *nitrocellulose*, is made from cotton or cellulose fibre. The violence of these explosives is tempered by mixing them with more or less inert or less active substances—*e.g.* when nitroglycerol is mixed with kieselguhr, *dynamite* results. The formation of smoke during the combustion of gunpowder is due to the presence of condensed water vapour and of solid compounds among the products of combustion—these solids also cause the fouling of the gun. With brown powder the smoke cloud clears much more quickly than with black powders due to the greater proportions of water vapour in the former. The so-called *smokeless powders* are of two classes: (i) mixtures of gun-cotton with some substance to regulate the combustion, or with some oxidizing material, but no nitro-glycerol; of (ii) mixtures of nitro-cellulose and nitro-glycerol with or without some material to regulate combustion. These explosives emit no solid product during explosion, although a faint cloud of condensed water vapour is produced.

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§ 38. Ammonium Nitrate

This salt was discovered by J. R. Glauber[1] in 1659; he prepared it by the action of nitric acid on volatile alkali—ammonium carbonate—and called it *nitrum flammans*. Ammonium nitrate is an artificial product, its occurrence in nature is quite exceptional. Ammonium nitrate, sulphate, and carbonate occur in small quantities in the atm. from which they are carried by rain and snow to the surface waters of the earth. A. Bobierre[2] measured the amount, month by month, in the air of Nantes; R. A. Smith determined the amount in the air of towns, etc., in Great Britain; C. Ochsenius, in the air of Paris; and A. Levy, and F. Fischer,

in the air of sewers. Selecting a few numbers from the published ammonia content of rain-water expressed in grams per cubic metre:

	Valentia.	Liverpool.	Manchester.	Glasgow.	Darmstadt.
NH_3	0·180	4·680	6·469	9·100	1·900
HNO_3	0·370	0·582	1·032	2·436	2·890

In localities where there is much sunshine, the proportion $NH_3 : HNO_3$ is less than in localities where there is less sunshine owing to the favourable influence of light on the oxidation of ammonia to the nitrate. The ammonium nitrate is formed in at least three ways: (i) The putrefaction of organic matter followed by the oxidation of the ammonia; (ii) the action of electric discharges on ammonia and water vapour; and (iii) the action of nitrifying bacteria on ammoniacal compounds.

The salt has been largely prepared by neutralizing aq. ammonia with nitric acid, and evaporating the soln. until a fine crystalline film appears on the surface, on cooling crystallization occurs. The ammonia is obtained as a by-product in the manufacture of coke, heating and lighting gas, in Mond's process for power gas from slack coal or peat, in the distillation of bastard coals and lignite; and as a direct product in the action of superheated steam on calcium cyanamide, and in the synthetic combination of hydrogen and nitrogen. The nitric acid is obtained by the action of sulphuric acid on sodium nitrate, by the fixation of atm. nitrogen in the electric arc flame, and by the catalytic oxidation of ammonia.[3]

Numerous patents have been taken for realizing the reaction: $(NH_4)_2SO_4 + 2NaNO_3 \rightleftharpoons Na_2SO_4 + 2NH_4NO_3$, but they have not been successful on account of the great solubility of the salts in water. In F. Benker's process, the double decomposition of ammonium sulphate by an eq. amount of sodium nitrate is conducted in very conc. soln. When the liquid is cooled to $-10°$ or $-15°$, sodium sulphate crystallizes out; the mother liquid is evaporated and cooled again. The liquid is separated from the sodium sulphate; mixed with a little nitric acid; and again cooled. A crop of crystals of ammonium nitrate is thus obtained. If desired, the salt can be freed from sulphates by treatment with baryta. V. Gröndahl and J. Landin extracted a mixture of ammonium sulphate and sodium nitrate with alcohol; C. Craig treated the mixture with conc. aqua ammonia; R. N. Lennox, and A. W. and J. A. Wahlenberg proposed to separate the ammonium nitrate from the mixture by distillation in vacuo. In C. Roth's process, ammonium sulphate and alkali nitrate are melted together between 160° and 200°, the alkali sulphate separates first from the cooling mass, and can be removed from the molten ammonium nitrate by a centrifuge.

In 1875, G. T. Gerlach proposed to treat the liquid obtained from the ammonia-soda process with sodium nitrate in a similar manner: $(NH_4)HCO_3 + NaNO_3 \rightleftharpoons NaHCO_3 + NH_4NO_3$, but, as shown by T. Fairley and G. Döllner, the incompleteness of the reaction prevented its industrial application. J. F. Chance, J. V. Skoglund, and T. Fairley[4] obtained patents for the process. R. Wedekind treated ammonium sulphate with rather less than the theoretical amount of calcium nitrate: $Ca(NO_3)_2 + (NH_4)_2SO_4 = CaSO_4 + 2NH_4NO_3$, the yield is quantitative, and the calcium sulphate can be readily separated. W. A. Dyes, and O. Nydegger and R. Wedekind have obtained patents in connection with this process. There are also patents in connection with the Norsk Hydro-Elektrisk-Kraelstof Aktieselshab for the preparation of ammonium nitrate by treating cyanamide, $CaCN_2$, with nitrous gases: $CaCN_2 + 2H_2O + 4HNO_3 = Ca(NO_3)_2 + CO_2 + 2NH_4NO_3$. E. Carez treated ammonium sulphate with barium nitrate; and C. A. Burghardt, with lead nitrate.

E. Rammann noted that a little ammonium nitrate is formed during the reduction of a soln. of ferric nitrate by metallic iron whereby ferrosoferric oxide is precipitated, and ammonium nitrate appears in the soln. E. W. von Siemens and J. G. Halske patented a process in which a mixture of well-dried oxygen, nitrogen, and ammonia

was exposed to the silent discharge and a deposit of ammonium nitrate was obtained on the walls of the vessel. W. Ostwald oxidized ammonia to ammonium nitrate by the agency of catalytic platinum; A. Frank and N. Caro proposed thorium oxide as catalyst; M. Wendriner, uranium compounds; and W. Traube and A. Biltz, cupric hydroxide. In 1908, the Deutschen Ammoniak-Verkaufs-Vereinigung, of Bochum, made 651 tons of ammonium nitrate by W. Ostwald's process; and in 1910, 1237 tons. C. T. Kingzett noted the formation of ammonium nitrate during the action of ozonized air on moist phosphorus; and, according to W. R. Hodgkinson and F. R. Lowndes, it is also formed during the combustion of ammonia in oxygen, and of hydrogen in the vapour of nitric acid. H. Davy observed the formation of ammonia at the cathode and of nitric acid at the anode during the electrolysis of water with air in soln., and R. Nithack has a process for the preparation of ammonium nitrate by electrolyzing water with nitrogen dissolved under a press. of 50 to 100 atm.

Ammonium nitrate can be readily obtained in columnar six-sided prisms or pyramids or in thin needles by careful evaporation and slow cooling; if evaporated to a very small bulk, it solidifies to a fibrous or dense mass. Some of the larger crystals can be bent, and this is accompanied by a crackling sound. At ordinary temp., the **crystals** are rhombic bipyramids. J. C. G. de Marignac,[5] V. von Lang, F. Wallerant, O. Lehmann, J. W. Retgers, etc., have measured the crystal angles, and, according to B. Gossner, the crystal parameters are: $a:b:c=0.9092:1:1.0553$. The rhombic form which is stable at ordinary temp. is very different in type from rhombic potassium nitrate, and the two salts are not isomorphous, although, as J. W. Retgers showed, the two salts are isodimorphous in forming two different types of rhombic mixed crystals according as one or other component predominates. J. W. Retgers also found that ammonium nitrate can form mixed crystals with rhombohedral sodium nitrate. Ammonium nitrate also forms two series of rhombic mixed crystals with silver nitrate. There is also a well-defined double salt: $NH_4Ag(NO_3)_2$. F. Wallerant, and M. Caillart have studied the mixed crystals of ammonium nitrate with the alkali and thallium nitrates.

The reported values for the **specific gravity** of the form which is stable at ordinary temp. range from 1·684 to 1·791. *H. Schiff and U. Monsacchi's*[6] *value is* 1·6973 at 23° (water at 4° unity); U. Behn's value at 20° is 1·725; J. W. Retgers' value is 1·725 at 15°; and the mol. vol. is 46·4 at 15°. L. Poincaré's value for the sp. gr. of the liquid, at 200°, is 1·36. G. Gerlach, F. Kohlrausch, W. Müller and P. Kaufmann, and many others have measured the sp. gr. of aq. soln. of ammonium nitrate. H. Gorke's results at different temp. are indicated in Table LX. (water at 4° unity).

TABLE LX.—SPECIFIC GRAVITIES OF SOLUTIONS OF AMMONIUM NITRATE.

Per cent. of salt.	0°	10°	18°	25°	40°	60°	85°	100°
2·00	1·011	1·0095	1·0072	1·0061	1·0016	0·9921	0·9781	0·9680
5·00	1·022	1·0210	1·0198	1·0183	1·0128	1·0032	0·9880	0·9780
10·00	1·046	1·0423	1·0405	1·0382	1·0335	1·0231	1·0095	0·9988
19·77	1·091	1·0868	1·0835	1·0805	1·0731	1·0628	1·0475	1·0372
30·33	1·1388	1·1341	1·1308	1·1271	1·1191	1·1088	1·0931	1·0830
40·15	1·186	1·1815	1·1778	1·1740	1·1662	1·1545	1·1381	1·1258
50·15	1·238	1·2320	1·2281	1·2240	1·2155	1·2030	1·1859	1·1755
59·94	1·293	1·2865	1·2813	1·2770	1·2673	1·2546	1·2385	1·2288

The soln. of ammonium nitrate in water is attended by a relatively large expansion. According to M. Rogow, if *w* grms. or one mol. of the salt be dissolved in 2000-*w* grms. of water, at 20°, there is a volume expansion of 47·6 c.c. H. Schiff and *U. Monsacchi* found at 23°:

Per cent. NH_4NO_3	63	42	28	14	7	4
Vol. 100 grms. soln.	77·1878	84·5479	89·4842	94·7000	97·4673	98·7103
Volume of components	74·2082	82·8297	88·6725	94·4583	97·3511	98·5334
Difference	*2·9796*	*1·7182*	*0·8117*	*0·2417*	*0·1162*	*0·1764*

The expansion thus has a minimum value with between 14 and 4 per cent. soln. According to R. Broom, the dilution of a soln. over 7 per cent. conc. is attended by a contraction. H. Schiff and U. Monsacchi found that the expansion in aq. soln. of nitric acid, potassium nitrate, or ammonium chloride is greater than with water. A. Geritsch, and H. Gilbault have also investigated this subject. J. W. Retgers found the mol. vol. of the salt in soln. is greater than 46·4, the value for the solid salt. E. Ruppin also found that the neutralization of an aq. soln. of ammonia by nitric acid is attended by a contraction in volume. G. T. Gerlach, and G. Tammann and W. Hirschberg measured the sp. gr. of ethyl alcohol soln.; and H. Schiff and U. Monsacchi, of methyl alcohol soln. H. Gilbault, V. Schumann, and W. C. Röntgen and J. Schneider have measured the **compressibility** of soln. of ammonium nitrate. The **surface tension** of aq. soln. of ammonium nitrate were measured by C. Forch,[7] who found that when σ represents the surface tension of the soln. at $\theta°$; σ_1, that of water; $w=\sigma-\sigma_1$; then, for soln. containing N-mols. of ammonium nitrate per litre at 14·5°–15·5°:

N	7·50	5·57	3·76	1·808	0·904
σ	8·745	8·487	8·252	8·047	7·941
σ/N	0·125	0·119	0·116	0·125	0·124

R. Abegg, A. Kanitz, and O. Pulvermacher have measured the **viscosity** of soln. of ammonium nitrate, and H. Gorke the reciprocal of the viscosity, *i.e.* the **fluidity** at different temp. (water at 25° unity), and his measurements are indicated in Table LXI. A. Kanitz also measured the viscosities of mixtures of ammonium nitrate with potassium, sodium, or barium nitrate, and found that the results follow the additive rule very closely. W. N. Bond studied the **plasticity** of crystals of ammonium nitrate.

TABLE LXI.—FLUIDITY OF SOLUTIONS OF AMMONIUM NITRATE.

Per cent. of salt.	0°	10°	18°	25°	40°	60°	85°	100°
0	0·5020	0·6840	0·8471	1·0000	1·360	1·901	2·663	3·150
2·00	0·510	0·6916	0·8595	1·016	1·368	1·870	2·583	3·051
5·00	—	0·7156	0·8728	1·012	1·365	1·842	2·475	2·85
10·00	0·5737	0·7492	0·9070	1·048	1·360	1·829	2·445	2·69
19·77	0·585	0·7055	0·9092	1·038	1·332	1·751	2·273	2·49
30·33	0·5920	0·7450	0·8616	0·0710	1·237	1·597	2·051	2·323
40·15	0·556	0·6789	0·7867	0·8850	1·104	1·409	1·779	2·010
50·15	0·415	0·5703	0·5698	0·7378	0·9104	1·140	1·441	1·617
50·94	—	0·4501	0·5204	0·5833	0·7345	1·9206	1·140	—

E. Maumené gave 153° for the **melting point,** V. H. Veley reported that the first signs of fusion occur at 150°, and that at 159°, the salt forms a clear liquid. M. Berthelot gave 152°; S. U. Pickering, 165°, 166°; H. Schiff and U. Monsacchi gave 166°; M. Bellati and R. Romanese, 168°; and O. Lehmann, 161°. R. G. Early and T. M. Lowry give 169·6° for the f.p. of the pure dry salt. The heating curve by J. Tollinger shows a steady rise up to 35·67°, and then falls to a minimum at 34·96° before rising again; while the cooling curve falls to 30·07° and then rises to 31·05°. There are also analogous changes on the heating curve at 86° and at 125°, and on the cooling curve at 82·5° and 124°. These changes are connected with changes in the morphological characters of the crystals. Both P. W. Bridgman and U. Behn noted that there is a marked hysteresis or lag in passing from one phase to another, and it is difficult to get the reaction to pass completely from

one phase to another. The reactions start with only a little sub-cooling or super-heating, but run to completion only with a much greater sub-cooling or super-heating.

At ordinary press. solid ammonium nitrate exhibits at least four transition temp. The molten salt freezes at about 168°, forming crystals of the modification **I-ammonium nitrate,** or ϵ-NH_4NO_3, which belong to the cubic system; at about 126°, the crystals become doubly refracting, pass into a second modification, δ-NH_4NO_3, or **II-ammonium nitrate,** which crystallizes in the tetragonal system —or possibly in the rhombohedral system. This form was discovered by M. L. Frankenheim in 1854. For the temp. of the I- to II-transformation, O. Lehmann gives 127°; M. Bellati and R. Romanese,[8] 124°–125°; S. Lussana, 124·9°–125·6°; W. Schwarz, 123·5°–125·6°; J. von Zawidzky obtained 125°; and K. Vogt, and R. G. Early and T. M. Lowry found 125·2° to be the best representative value. A second transformation occurs at about 83°, and the crystals become *optically biaxial, forming a third modification,* γ-NH_4NO_3, or **III-ammonium nitrate,** belonging to the monoclinic system. These crystals appear to be almost tetragonal, so that F. Wallerant called them *monocliniques quasi-quadratiques*. For the temp. of the II- to III-transformation, O. Lehmann gives 87°; U. Behn, 83°; M. Bellati and R. Romanese, 82·5°–86°; W. Schwarz, 82·5°–86·5°; F. Wallerant, 82°; G. Tammann, 84·6°; S. Lussana, 85·85°; J. von Zawidzky, 85·4°; and K. Vogt, 82·26°. R. G. Early and T. M. Lowry believe 84·2° as the best representative value. A third transition occurs at about 32°, the crystals then become rhombic—*quasi-quadratiques*—forming **IV-ammonium nitrate,** or β-NH_4NO_3. This IV-modification is the stable form at atm. temp., and is the variety ordinarily occurring in commerce. For the temp. of the III- to IV-transformation, O. Lehmann gives 36°; *M. Bellati and R. Romanese,* 31°–35°; W. Schwarz, 31°–35°; F. Wallerant, 32°; U. Behn, 32°; G. Tammann, 31·8°; S. Lussana, 30·55°–34·45°; and W. Müller, 32·2°; while R. G. Early and T. M. Lowry believe 32·1° to be the best representative value. G. Tammann found a fourth transition at −4°, but afterwards noted that his first record was in error, and placed the transition temp. at −16°. The best representative value for this transition point may be taken as −18°. The crystals of the modification **V-ammonium nitrate,** or α-NH_4NO_3, belong to the tetragonal system; and have a positive double refraction a little weaker than the II-variety. For the temp. of the IV- to V-transformation, F. Wallerant gives −14° to −16°; and U. Behn, −18°. The latter number is taken to be the best representative value. To summarize, the best representative values of the transition points are:

$$\underset{\text{Liquid}}{NH_4NO_3} \overset{169\cdot6^\circ}{\rightleftharpoons} \underset{\text{Cubic}}{\text{I-}NH_4NO_3} \overset{125\cdot2^\circ}{\rightleftharpoons} \underset{\text{Tetragonal}}{\text{II-}NH_4NO_3} \overset{84\cdot2^\circ}{\rightleftharpoons} \underset{\text{Monoclinic}}{\text{III-}NH_4NO_3} \overset{32\cdot1^\circ}{\rightleftharpoons} \underset{\text{Rhombic}}{\text{IV-}NH_4NO_3} \overset{-18^\circ}{\rightleftharpoons} \underset{\text{Tetragonal}}{\text{V-}NH_4NO_3}$$

Neither O. Lehmann (1906) nor U. Behn could detect any signs of further transformation between −18° and −140°. R. G. Early and T. M. Lowry show that the velocities of the higher transition temp. are fast enough to give sharply-defined breaks in the heating and cooling curves, but the transition temp. at 32·1° cannot be determined in this way because of the slowness of the change. Dilatometric methods were used. The velocity of the change v at the temp. θ can be represented by $\pm(\theta-\theta_0)=k\log_{10}(\sqrt{v}+1)$, where θ_0 denotes the transition temp., and v, the percentage amount changed per hour—when $v=2\cdot5$, $\pm(\theta-\theta_0)=0\cdot41$.

Modification II and V are so much alike that F. Wallerant suggested that they are identical. He said: "Il n'y aurait rien de surprenant dans l'existence de deux modifications appartenant au même système et parallèlement orientées. . . . Mais bien plus il n'y a en réalité qu'une modification stable dans deux intervalles de température." If this hypothesis were to be verified the phenomenon would be unique. No case is known where the crystals of a single definite substance, presenting the same crystalline form with all the physical properties identical, can exist within two separate ranges of temp.

U. Behn has pointed out that if II and V be identical, the following reversible cycle can be performed: Transform a gram of the salt at 83° into III, cool it to 32°, and transform it to IV, and cool it to −18°, and transform it to V. Finally, heat this back to 83°. The series of changes produces Q_3 cals. at 83° (θ_3), Q_4 cals. at 32° (θ_2), and Q_5 cals. at −18° (θ_5). The sp. ht. of the modification in the order named are C_3, C_4, and C_5. Then:

$$Q_3+\int_{\theta_4}^{\theta_3}C_3d\theta+Q_4+\int_{\theta_5}^{\theta_4}C_4d\theta+Q_5=\int_{\theta_5}^{\theta_3}C_5d\theta \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The identity of the II and V modification does not here involve the vanishing of the sums of the heats of transformation: $Q_3+Q_4+Q_5=0$, for this could occur only if

$$\int_{\theta_4}^{\theta_3}C_4d\theta+\int_{\theta_5}^{\theta_4}C_4d\theta=\int_{\theta_5}^{\theta_3}C_5d\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

for $Q_3+Q_4+Q_5$ can be zero when each of the heats of transition is zero—they cannot each be negative. If the modifications II and V are identical the average sp. ht. between −18° and 83° would have to be much higher than it is at either of these two temp. By introducing the known data into (1) there is a difference of 8·4 cals. in the two sides of the equation. There is an uncertainty in the value of C_5, but it is hardly likely to amount to 8·4 cals. Hence, it is probable, but not certain, that the two forms are not identical.

F. Wallerant added different proportions of isomorphous cæsium nitrate to ammonium nitrate, and found that the tetragonal modification could be stable not only above 83° but below −18°, and also throughout the whole intermediate range of temp. This does not prove that the II- and V- varieties are identical, for a transition may occur without obvious physical change. U. Behn examined the two tetragonal modifications dilatometrically, thermally, and crystallographically, but was unable to establish precise proof of the identity or otherwise of the II- and V- varieties of this salt. The general trend of the evidence, however, is against the hypothesis that the two forms are identical. M. Caillart examined the mixed crystals of ammonium and potassium nitrates and found (1) rhombic crystals of the potassium nitrate type containing 0–17·2 mol. of ammonium nitrate per 100 mol. of mixture, (2) monoclinic crystals with 55–94·5 mol. of ammonium nitrate per 100 mol. of mixture, and (3) rhombic crystals of the ammonium nitrate type with 98–100 mol. of ammonium nitrate per 100 mol. of mixture.

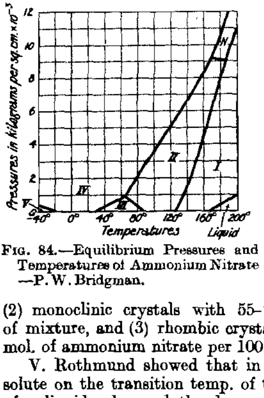

FIG. 84.—Equilibrium Pressures and Temperatures of Ammonium Nitrate —P. W. Bridgman.

V. Rothmund showed that in the general case of solid soln., the effect of a solute on the transition temp. of the solvent is analogous to the cryoscopic effect of a liquid soln., and the depression of the transition temp. is given by $\theta_0-\theta_1=RT^2/Q(C_2-C_1)$, where θ_0 and θ_1 denote the transition temp. of ammonium nitrate before and after the addition of potassium nitrate; T, the absolute transition temp. of ammonium nitrate alone; C_0 and C_1, the mol. conc. of potassium nitrate in 100 grms. of the two modifications of ammonium nitrate, and Q is the heat of transformation of ammonium nitrate. The results with potassium and ammonium nitrates are in accord with V. Rothmund's rule, and, at 32°, there is a change of quadruple into triple molecules: $3(NH_4NO_3)_4 \rightleftharpoons 4(NH_4NO_3)_3$.

S. Lussana, G. Tammann, and P. W. Bridgman have measured the effect of press. on the transition points. The results of the last-named investigator are shown in Fig. 84. According to R. Clausius' equation, $dT/dp=T.dv/Q$, the variation of the transformation temp. dT with a change of press. dp is positive when dv is positive and negative when dv is negative. Q represents the quantity of heat—taken negative—which is liberated when a stable system has its temp. raised,

and is thereby transformed into another stable system with the accompanying change of volume dv. The fusion point of the salt at one kgrm. per sq. cm. press. is 168°, and 202° when the press. is 1000 kgrms. per sq. cm., dv is then 0·051 ± c.c. per grm.; dT/dp, 0·034; the latent heat, 6·9 kgrm. m. per grm.; and the change of energy, 6·6 kgrm. m. per grm. The following data are selected from those compiled by P. W. Bridgman:

At the transition points I to II, 125·5° at one kgm. per sq. cm. press., dv 0·01351 c.c. per grm., dT/dp is 0·00974; and the latent heat and change of energy are each 5·53 kgrm. m. per grm. At a press. of 9000 kgrms. per sq. cm., the transition point is 186·6°, dv, 0·00476 c.c. per grm.; dT/dp, 0·00409; and the latent heat and change of energy are respectively 5·35 and 4·92 kgrm. m. per grm. For the II to III transition point, at 82·7° at one kgrm. per sq. cm. press., $dv = -0·00758$. $dT/dp = -0·0159$; and the latent heat and change of energy are each 1·70 kgrm. m. per grm.; at 9000 kgrms. per sq. cm. press., the transition temp. is 167·4°, $dv = -0·01265$; $dT/dp = -0·0111$; and the latent heat and change of energy are respectively 5·01 and 3·87 kgrm. m. per grm. The transition point III to IV is 32·0° at 1 kgrm. per sq. cm. press., and $dv = 0·02026$; dT/dp 0·0311, and the latent heat and change of energy are each 1·99 kgrm. m. per grm. The transition point is 60·8° at 800 kgrms. per sq. cm. press.; $dv = 0·02128$; dT/dp 0·0410; and the latent heat and change of energy are respectively 1·73 and 1·56 kgrm. m. per grm. The IV to V transition point is −18·0° at one kgrm. per sq. cm. press. when dv 0·017 ± dT/dp 0·063, and the latent heat and change of energy are each 0·69 kgrm. m. per grm. P. W. Bridgman sought if the falling IV to V transition curve is replaced by the appearance of another phase with a rising curve between IV and the new modification, but obtained negative results with press. up to 12,500 kgrms. per sq. cm. at room temp.

P. W. Bridgman found a sixth modification, **VI-ammonium nitrate,** whose range of stability on the pT-curves is shown in Fig. 84. The transition temp. I to VI are 186·6° and 201·6° respectively at 9000 and 11,000 kgrms. per sq. cm. press.; the corresponding values of dv are 0·00858 and 0·00740; the latent heat and change of energy respectively 5·26 and 4·49 kgrm. m. per grm. for the smaller press., and 4·68 and 3·87 kgrm. m. per grm. for the larger press.; and dT/dp is 0·00750. For the II to VI transformation respectively at 9034 and 9154 kgrms. per sq. cm. press., the transition temp. are respectively 185° and 170°; dv, 0·00373 and 0·00312; $dT/dp = -0·125$; and the latent heat and change of energy respectively 0·111 and 0·296 kgrm. m. per grm. for the higher press., and 0·137 and 0·474 kgrm. m. per grm. for the lower press. Similarly, for the VI to IV transformation, the transition temp. are 167·9° and 192·5° respectively for press. 9000 and 12,000 kgrms. per sq. cm., the corresponding values of dv are 0·00959 and 0·00950; $dT/dp = 0·00820$; and the latent heat and change of energy respectively 5·16 and 4·29 kgrm. m. per grm. at the lower press., and 5·40 and 4·25 kgrm. m. per grm. at the higher press.

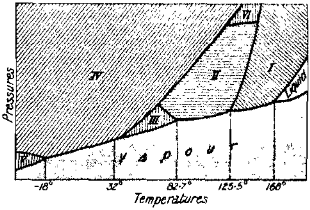

FIG. 85.—Diagrammatic Representation of the Different Forms of Ammonium Nitrate.

The triple point for II–III–IV ammonium nitrates is 63·3° at 860 kgrms. per sq. cm. press.; for I–II–VI ammonium nitrates, 186·7° at 9020 kgrms. per sq. cm. press.; and for II–IV–VI ammonium nitrates, 169·2° at 9160 kgrms. per sq. cm. press. At the triple points, the values of dv c.c. per grm., dT/dp, and of the latent heat and change of energy in kgrm. m. per grm. are respectively: III–IV, 63·3°−0·02135, 0·0417, 1·72, and 1·54; II–III, 63·3°−0·00925, 0·0294, 1·06, and 1·14; II–IV, 63·3°−0·1210, 0·0146, 2·78, and 2·68; I–II, 186·7°−0·00475, 0·00406, 5·38, and 4·95; I–VI, 186·7°−0·00855, 0·00750, 5·24, and 4·47; II–VI, 186·7°−0·00380, −0·125, 0·14, and −0·48; II–IV, 169·2°−0·01267, 0·0111, 5·06, and 3·91; II–VI, 169·2°−0·00309, −0·125, 0·11, and 0·38; and for IV–VI, 169·2°−0·00958, 0·00820, 5·17, and 4·29. P. W. Bridgman also measured the velocity of the transformation of the different forms of ammonium nitrate.

The pT-relations of the six different forms of ammonium nitrate are illustrated diagrammatically in Fig. 85. M. Bellati and R. Romanese, and U. Behn measured the changes in volume at atm. press. at the four transition points. M. Bellati and R. Romanese have also measured the latent heats of the transformation III–IV, III–II, and II–I. U. Behn found the latent heat of transformation at −18° to be 1·62. M. Bellati and R. Romanese give for the heat of transformation

at 32°, 5·02; and at 83°, 5·33. P. W. Bridgman's values are indicated above. G Tammann has measured the co-ordinates of the triple points II–III–IV.

The **thermal expansions** in c.c. per gram of some of the different forms of ammonium nitrate have been measured by M. Bellati and R. Romanese, U. Behn, and P. W. Bridgman. U. Behn measured the coeff. of expansion of the solid between −60° and 100° and found:

−60°	−20°	0°	18°	20°	60°	100°
0·000677	0·000852	0·000920	0·000978	0·000982	0·001069	0·001113

H. Kopp gave 0·000973 at 20°, and M. Bellati and R. Romanese 0·000963 at 20°. U. Behn also represented the volume v at $\theta°$ between 100° and −40° by the equation $v=v_0(1+0·000922+0·00000163\theta-0·0000000045\theta^2)$. M. Bellati and L. Finazzi give for the coeff. of cubical expansion at 20°, 0·00005633; and at $\theta°$ between 86° and 125°, $v=v_0(1+0·0_5477\theta+0·0_53680\theta^2)$; and between 125° and 139·3°, $v=v_0(1-0·0_35659\theta+0·0_53680\theta^2)$. For the II-modification, M. Bellati and R. Romanese give 0·0001165, and U. Behn gives 0·00041 c.c.; for III, the former give 0·000134, the latter gives 0·00036; for IV, the former give 0·000222, and the latter gives 0·00048. U. Behn's results agree with those of P. W. Bridgman, who makes II expand 0·000038 c.c. per gram more than III; and IV expand 0·000115 c.c. per gram more than III. Hence, IV is more expansible than III, which is stable at a higher temp.—this is unusual. U. Behn gives for the V-modification 0·00037 c.c. per gram. The coeff. of expansion of aq. soln. has been measured by C. Forch,[9] N. A. Tschernay, and by S. de Lannoy. *Vide* also alkali nitrates. S. de Lannoy found for the volume v at $\theta°$ $v=(v_0+\delta v)10^{-5}$.

Per cent. NH_4NO_3	20°	40°	60°	80°
4	282	995	1882	3015
12	549	1338	2312	3475
20	718	1600	2633	3825
44	948	1960	3058	4240

M. Bellati and R. Romanese give for the **specific heats** in calories per gram, at atm. press., II, 0·426; III, 0·355; and IV, 0·407. U. Behn found the sp. ht. between −15° and 15° to be 0·395 between −79° and −20°, 0·352; between −190° and ordinary temp., 0·305; from −190° to −20°, 0·274. The sp. ht. of the V-modification may be taken as $0·423+0·001430\theta$ between −190° and 20°; and for the mean sp. ht. of the IV-variety between 0° and 31°, 0·407; or at $\theta°$ within this temp. range, $0·395+0·000750\theta$. The sp. ht. of aq. soln. has been measured by A. Winkelmann, J. Thomsen, and J. C. G. de Marignac. The composite results from about 18° to about 50° are:

Per cent. salt	64	47·1	28·6	15·1	9·1	2·9
Sp. ht.	0·6102	0·697	0·7227	0·8797	0·9249	0·9654

Solid ammonium nitrate is very deliquescent in moist air, and it is very soluble in water. According to H. Lescœur[10] and F. L. Kortright, at 20°, the salt absorbs moisture from the air if the vap. press. of the water is over 9 mm. The vap. press. of a sat. soln. has the same value. It is very difficult to dry the salt; it can be obtained with less than 0·1 per cent. of moisture by exposure over phosphorus pentoxide at ordinary temp. in a desiccator. U. Behn observed a slight decomposition of the salt after it had stood a few days in the desiccator. This was evidenced by the smell of nitrogen oxides. If heated, the decomposition is quicker. If one limb of a U-tube containing the salt be heated to 100°, and the other limb be cooled to −79°, water is continuously collected, but the salt becomes no drier.

G. Tammann measured the vap. press. of soln. of 5·02, 53·25, 118·51, and 192·93 grms. of ammonium nitrate in 100 grms. of water at 100°, and found the **lowering of the vapour pressure** to be respectively 14·6, 132·1, 235·9, and 324·3 mm. E. B. R. Prideaux and R. M. Caven measured the vap. press. of 47·8 per cent., 60·4 per cent., and sat. soln. of ammonium nitrate, and represented the vap. press.,

p, at $\theta°$, of a 4·8 per cent. soln. by $p=336·5-12·845\theta+0·15116\theta^2$; of a 60·4 per cent. soln. by $p=231·2-9·66\theta+0·125\theta^2$; and of a sat. soln. by $p=16-0·8275\theta+0·01525\theta^2-0·06875\theta^3$. Accordingly, the values of dp/dT are respectively $-12·845+0·30232\theta$, $-9·666+0·25\theta$, and $-0·8275+0·0305\theta-0·020625\theta^2$. The first named also studied the deliquescence and drying of this salt. The sp. vol. of steam can be calculated from pv-equations for steam, and hence, the **latent heat of evaporation,** Q, is $Q=T(v_2-v_1)dp/dT$, so that for the unsaturated soln. Q is 450 to 500 cals., about 50 cals. less than for water at the same temp., and it appears to attain a maximum between 60° and 70°. The latent heat of evaporation of sat. soln. of those salts whose solubilities increase continuously with rise of temp. will generally become zero when the press. of the sat. vap. reach a maximum for which $dp/dT=0$, and thereafter become negative when the evaporation of water with the precipitation of the salt evolves heat. The temp. of zero latent heat of a sat. soln. is estimated at 112°. For sat. soln. of ammonium nitrate:

	40°	45°	50°	60	70°	80°	90	95°
p cm. . . .	2·9	3·6	4·4	6·4	9·2	12·2	14·8	16·0
Q cals. . . .	372	404	397	444	367	269	210	170

G. T. Gerlach found the **boiling point** of a soln. of 10, 439, 4099, and ∝ grms. of salt in 100 grms. of water to be respectively 101°, 130°, 200°, and 240°. J. Legrand obtained higher b.p. than these. The result, however, cannot be very exact because of hydrolysis, and decomposition—particularly over 130°. E. H. Loomis, and H. C. Jones and B. P. Caldwell measured the **lowering of the freezing point** of soln. of ammonium nitrate containing 0·0801, 4·006, and 18·072 grms. of salt in 100 c.c. of soln., and found the respective depressions to be 0·0358°, 1·629°, and 8·720°; and the mol. lowering of the f.p. respectively 3·6°, 3·26°, and 2·91° respectively. Other determinations have been made by F. Guthrie, F. Rüdorff, J. Tollinger, F. M. Raoult, and L. C. de Coppet. The latter found the cryohydric temp. −17·35 with a soln. containing 70 grms. of salt in 100 grms. of water. F. Guthrie found −17·2° for a soln. with 78 grms. of salt and 100 grms. of water.

J. Thomsen's values [11] for the **heat of formation,** $(NH_{3gas},HNO_3)=34·7$ Cals., and $(N_2,2H_2,1\frac{1}{2}O_2)=88·1$ Cals.; and M. Berthelot's value for the last-named result is 87·9 Cals., and for $(N_2O,2H_2O_{liquid})=-29·5$ Cals. The **heat of neutralization** of ammonia and nitric acid in dil. soln. is 12·3 Cals., according to J. Thomsen, and 12·5 Cals., according to M. Berthelot; T. Andrews found 12·44 Cals. The soln. of ammonium nitrate in water is attended by a considerable absorption of heat. According to F. Rüdorff, the soln. of 60 parts of salt in 100 parts of water lowers the temp. from 13·6° to −13·6°, *i.e.* about 27°; and if the water is initially at 0°, ice separates out during the dissolution of the salt, for the temp. falls to −16·7°. This property is utilized in preparing the freezing mixture: Ammonium nitrate 5, sodium chloride 5, snow 12, which is capable of producing a temp. of −32°. J. Thomsen found the **heat of solution** of a mol. of this salt in 200 mols. of water to be 6·322 Cals.; and, according to M. Berthelot, 6·20 Cals. in 220–240 mols. of water at 10·15°. The heat of soln., at 0°, with p per cent. of salt between 5·04 and 20 per cent. is, according to A. Winkelmann, $92·25-1·737p+0·0402p^2$; and between 20 and 40 per cent., $89·1-0·985p+0·0105p^2$. J. Thomsen gives for the **heat of dilution** by n-mols. of water to a soln. containing $2NH_4NO_3+5H_2O$ at about 18°:

n . . .	1	5	15	35	95	195	395
Cals. . .	−0·67	−1·28	−2·52	−3·58	−4·58	−5·02	−5·23

T. Graham, F. R. Pratt, A. Winkelmann, and J. Tollinger have also investigated this subject. The integral heat of soln., *i.e.* the heat absorbed in producing a sat. soln., is −4 Cals. They also found the theoretical heat of soln. to be −3·6 Cals.; and the heat of soln. of the first mol. in 200 mols. of water, −6·3 Cals.

H. C. Jones and F. H. Getman,[12] and F. L. Haigh have measured the **refractive**

indices of aq. soln. of ammonium nitrate, and found for soln. of 0·05, 0·50, 1·00, and 2·00 mols. per litre the respective values 1·32538, 1·32989, 1·33485, and 1·34449—*vide* alkali nitrates. According to J. H. Gladstone and W. H. Perkin, the **molecular magnetic rotation** of the dissolved nitrate is 2·316, and the **molecular refraction** for the *A*-line, according to Gladstone and Dale's formula, is 25·23; the **molecular dispersion** for the *H*- and *A*-lines is 1·88. O. Humburg also measured the mol. rotation of aq. and methyl alcohol soln.; and D. Dijken, the mol. refraction and dispersion. E. Doumer gives the mol. refraction 18·8. O. Reinkober studied the reflexion spectrum for **ultra-red rays.**

According to L. Poincaré,[13] the sp. **electrical conductivity** of the molten salt at 172°, 202°, and 213° is respectively 0·320, 0·397, and 0·447 reciprocal ohms; and at $\theta°$ between 160° and 220° is $0·400\{1+0·0073(\theta-200)\}$ reciprocal ohms. The sp. gr. of the fused mass is 1·36 at 200°, so that there are 18·8 mols. per litre, and the mol. conductivity is therefore 233 at 200°. Numerous measurements have been made of the electrical conductivity of aq. soln. There are the measurements of J. H. Long, R. Lenz, E. Bouty, S. Arrhenius, F. Kohlrausch, W. Foster, O. Grotrian, etc. H. C. Jones and co-workers found the eq. conductivity λ between 0° and 35° for soln. with an eq. of the salt in v litres of water. At 25°, and λ_∞ 137·8,

v	1	2	4	10	40	100	400	1000	2000
λ	68·1	73·3	77·7	83·1	89·6	92·0	95·6	99·6	100·00

H. Gorke measured soln. between 2 and 60 per cent. conc., and between 0° and 100°. F. Kohlrausch and O. Grotrian give for the temp. coeff. of a 49·3 per cent. soln., a specific conductivity of $K_0(1+0·0235\theta+0·000019\theta^2)$, where K_0 represents the specific conductivity at 0°. R. Dennhardt measured the relation between the viscosity and electrical conductivity. M. le Blanc found the **decomposition potential** of a *N*-soln., with platinum electrodes, at room temp., to be 2·08 volts, being thus about 0·08 volt less than the value for potassium and sodium nitrates.

S. Arrhenius found the conductivity λ_0 of a salt in water is reduced to λ when x per cent. by volume of a non-electrolyte is added, where $\lambda=\lambda_0(1-\frac{1}{2}ax)^2$, where a is a constant:

	Methyl alcohol.	Ethyl alcohol.	Isopropyl alcohol.	Ether.	Acetone.	Cane sugar.
a	0·0157	0·0219	0·0246	0·0181	0·0141	0·0279

O. Humburg measured the conductivity in methyl alcohol soln.

The percentage **degree of ionization** α of aq. soln. of ammonium nitrate has been calculated from the cryoscopic and conductivity measurements of E. H. Loomis, H. C. Jones and B. P. Caldwell, and W. Kistiakowsky of *N*-soln. of ammonium nitrate, are:

N	0·001	0·01	0·1	1·0	2·0	3·0	4·0
α (cryoscopic)	—	95	85	70	53	41	31
α (conductivity)	98·4	90	82	71	63	59	56

The agreement for 2*N*- and more conc. soln. is not good. Ammonium nitrate behaves as a strong electrolyte with respect to W. Ostwald's dilution law. H. Gorke obtained better agreement by allowing for the change of ionic mobility with the more conc. soln. owing to the decreased fluidity of the medium. He substituted the term $\lambda F_0/F$ in place of λ, where F_0 represents the fluidity of the water, and F that of the soln. Ammonium nitrate in aq. soln. is but feebly hydrolyzed, but the hydrolysis is recognizable when the soln. is heated. H. C. Dibbits showed that the **hydrolysis** can be detected at ordinary temp., as is also the case with other ammonium salts, by passing a stream of air through the soln. V. H. Veley, and E. G. Hill measured the degree of hydrolysis relatively with other ammonium salts, but the results were obscured by secondary reactions. C. Brück has studied the hydrolysis of boiling soln. of ammonium nitrate.

Determinations of the **solubility** of ammonium nitrate in water for a few temp.

were obtained by C. J. B. Karsten, T. T. Harris, G. J. Mulder, F. Rüdorff, etc.[14] W. Schwarz said that at 25°, the solubility decreases with a rise of temp., but W. Müller and P. Kaufmann show that this is not correct; there are, however, definite breaks in the continuity of the solubility curve corresponding with the changes in the character of the solid on a rising temp. Solubility determinations by L. C. de Coppet below 0°; by W. Müller and P. Kaufmann between 60° and 74·8°; by W. Schwarz between 50° and 125·6°, are summarized in Fig. 86.

	0°	20·2°	2·5°	50°	70°	80°	90°	100°
Per cent. NH_4NO_3 . .	54·19	65·80	72·0	77·40	83·32	85·3	88·1	89·71

The data by the different observers are not very concordant, presumably because the soln. were in some cases partially sat., and possibly also because of the incompleteness of the transformations from one form to another. C. J. B. Karsten, F. Rüdorff and A. A. Noyes measured the effect of the addition of other salts on the solubility of ammonium nitrate. Expressing the results in mols. per litre, at 19·5°, a sat. soln. contains 5·44 of ammonium chloride and 21·7 of the nitrate while if these salts are present alone, the solubilities are respectively 6·93 and 25·0. Similarly with sodium nitrate at 16°, a sat. soln. has 9·07 of sodium nitrate, and 20·4 of ammonium nitrate when the solubilities of the individual salts are respectively 9·76 and 24·0. Similarly, 100 grms. of water, at 20°, will dissolve 162·9 grms. of ammonium nitrate and 77·1 grms. of sodium nitrate; or 88·8 grms. of ammonium nitrate and 40·6 grms. of potassium nitrate; or 101·3 grms. of ammonium nitrate and 6·2 grms. of barium nitrate. For the solubility in ammonia and in nitric acid soln.—*vide infra*.

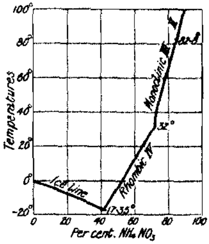

FIG. 86.—Solubility Curve of Ammonium Nitrate.

J. J. Pohl[15] found 100 parts of 66·8 per cent. *ethyl alcohol* dissolved 43·7 parts of ammonium nitrate at 25°, and 91 parts when boiling. Determinations have been made by C. A. L. de Bruyn, H. Schiff and U. Monsacchi, etc. G. T. Gerlach and G. Tammann and W. Hirschberg measured the sp. gr. of ethyl alcohol soln. A. Fleckenstein's data for the solubility of the salt in 100 parts of solvent—methyl or ethyl alcohol—are shown in Tables LXII and LXIII. The solubility in *methyl*

TABLE LXII.—SOLUBILITY OF AMMONIUM NITRATE IN ETHYL ALCOHOL-WATER (A. FLECKENSTEIN).

Alcohol (per cent.).	30°	35°	40°	45°	50°	55°	60°	65°	70°	75°	80°
100	3·8	4·5	5·25	5·9	6·4	7·0	7·7	8·2	8·9	9·5	10·1
93·69	8·8	9·8	11·0	12·0	13·1	14·5	15·8	17·8	20·2	23·1	26·0
86·77	13·5	16·2	18·8	21·2	24·0	27·0	30·3	34·5	40·0	47·2	55·0
76·12	30·2	35·1	40·5	46·5	53·6	62·0	71·0	8·10	—	—	—
62·82	60·6	69·5	79·5	91·4	104·0	116·6	—	—	—	—	—
51·65	—	102·0	114·0	138·0	144·0	161·5	181·4	205·0	—	—	—
40·87	120·2	136·4	152·8	170·0	189·6	213·0	240·5	271·4	—	—	—
25·81	—	179·0	196·0	217·0	242·5	272·0	310·0	—	—	—	—
0	231·0	254·0	277·0	314·0	—	—	—	—	—	—	—

alcohol is thus greater than in ethyl alcohol. The change in the solubility of the salt in ethyl alcohol with a rise of temp. is small and linear; with methyl alcohol, the solubility increases faster than the temp. Additions of ethyl alcohol to water lower the solubility of ammonium nitrate, while additions of methyl alcohol raise

the solubility of the salt. H. Schiff and U. Monsacchi have measured the sp. gr. of the soln. in methyl alcohol; O. Humburg, the molecular magnetic rotation, and the conductivity. W. H. Krug and K. P. McElroy found ammonium nitrate to be very soluble in *acetone*.

TABLE LXIII.—SOLUBILITY OF AMMONIUM NITRATE IN METHYL ALCOHOL-WATER (A. FLECKENSTEIN).

Alcohol (per cent.).	30°	35°	40°	45°	50°	55°	60°
100	20·0	22·8	25·1	28·0	31·5	35·4	39·6
83·75	41·0	47·2	54·4	62·3	71·6	82·0	94·0
73·64	60·0	70·1	81·0	92·5	105·0	119·0	135·6
60·39	92·5	105·0	118·3	134·0	151·0	169·8	190·4
53·23	117·2	133·0	150·5	169·5	191·0	215·0	242·0
24·83	—	200·0	221·0	244·0	270·3	299·0	—
0	231·0	254·0	277·0	314·0	—	—	—

Like other ammonium salts, the nitrate gives off ammonia and becomes acid when exposed to the air or when heated, and as J. P. Emmet[16] showed, it then possesses an acid reaction: $NH_4NO_{3solid}=HNO_3+NH_3-41·3$ Cals. Molten ammonium nitrate decomposes into nitrous oxide and water: $NH_4NO_3 \rightarrow N_2O+2H_2O$. According to M. Berthelot, the heat of decomposition of the solid is 29·5 Cals. at constant press. (liquid water), with gaseous water the heat of the reaction is 10·2 Cals.; according to J. Thomsen, the heat of the reaction at constant press. (liquid water) is 30·26 Cals. S. U. Pickering noted that the development of gas bubbles can be first detected between 185° and 186°; V. H. Veley, at about 210°; W. Smith, at about 170°; J. Legrand, 190°–200°. A. Pleisch found that the gas is copiously evolved at 250°, and some salt sublimes unchanged, and J. Legrand says that the salt boils without decomposition at 180°. J. H. Niemann found that ammonium nitrate is decomposed by heat when it is confined in a tube under press. If the temp. does not rise above 200°, some salt escapes decomposition by subliming to the cooler parts of the containing vessel in fine crystals. According to R. Reik, the salt can be distilled without decomposition in vacuo, and it then boils at 210°. V. H. Veley found that the rate of decomposition of ammonium nitrate into nitrous oxide and water is dependent not only upon the mass of salt undergoing decomposition, but also upon the proportion of free nitric acid present. If the reaction of the salt be rendered alkaline at starting, the rate of decomposition gradually increases, while the proportion of free acid increases; a period of maximum velocity is then reached, corresponding to the greatest proportion of free acid; from this point the rate decreases very slowly, while the proportion of free acid also decreases. An excess of ammonia obtained either by passing in the gas, or by the addition of a basic oxide, will completely stop the reaction, even at temp. 50°–60° above the normal point of its decomposition. If the reaction of the salt be rendered acid at starting, the rate of decomposition gradually decreases, while the proportion of acid gradually decreases. After heating the salt for about 13–16 hours, the rate of change becomes practically constant. V. H. Veley also found that the speed of the reaction is augmented in the presence of finely divided glass dust, graphite, etc. L. A. Buchner says that spongy platinum accelerates the decomposition of the fused salt with the evolution of nitric oxide alone. N. A. E. Millon and M. J. Reiset found that when platinum black is mixed with the salt, nitrogen is given off by the decomposing mass—according to M. Berthelot, by the side reaction: $5NH_4NO_3=4N_2+9H_2O+2HNO_3$. E. B. R. Prideaux and R. M. Caven have found that the hydrolysis of ammonium nitrate which occurs when an aq. soln. of this salt is evaporated in an acid-resisting vessel is very small and the loss is consequently inappreciable. There is considerable loss of ammonia when ammonium nitrate

soln. is evaporated in contact with iron, accompanied by corrosion of the iron and consequent pollution of the residual salt. This is due to interaction between the iron and the hydrolytic nitric acid, with concomitant loss of ammonia. The substitution of aluminium for iron as the material of the containing vessel almost entirely obviates loss of ammonia because of the inertness of this metal towards nitric acid.

In addition to the three modes of decomposition just indicated the salt can also decompose into nitrogen peroxide, nitrogen, and water. $4NH_4NO_{3solid}=3N_2+N_2O_4+8H_2O+29.5$ Cals. There is also a possible formation of nitrogen trioxide: $3NH_4NO_{3solid}=2N_2+6H_2O_{liquid}+N_2O_3+42.5$ Cals. If the salt be superheated, especially from 230° upwards, the decomposition becomes more and more rapid, and ends by becoming explosive at the same time as the salt becomes incandescent. According to M. Berthelot, the explosive reaction: $2NH_4NO_3=2N_2+4H_2O+O_2$, is brought about by suddenly heating the salt to a very high temp. under great press., and it requires a strong detonator—*e.g.*, according to C. A. L. de Bruyn, by mercury fulminate; the explosive reaction: $2NH_4NO_3=N_2+2NO+4H_2O$, occurs with the aid of a weak detonator; while the reaction: $NH_4NO_3=N_2O+2H_2O$, occurs when the salt is gradually heated without any marked increase of press. M. Berthelot also found that the product of the heat of the reaction, Q_v, with the volume of gas—V litres—produced in the reaction (water as vapour), represents the maximum work performed by the explosion. For the first named reaction, $Q_v=421$ Cals., $V=976$, and $Q_vV=411,000$; for the second reaction, $Q_v=140$ Cals., $V=976$, and $Q_vV=137,000$; and for the third reaction, $Q_v=151$ Cals., $V=836$, and $Q_vV=126,000$. This agrees with facts in so far as the first of the three explosive reactions is the most violent, and the last-named reaction least violent. There are thus, at least, seven different ways in which ammonium nitrate can decompose—some of these proceed as concurrent or side reactions. J. J. Berzelius, for instance, says that if heated so strongly that the vessel becomes filled with white fumes, nitric oxide, ammonium nitrate, and free ammonia are evolved as well as nitrous oxide. When rapidly heated by throwing the powdered nitrate on a red-hot porcelain plate or red-hot crucible, it burns with a very slight noise—hence the old name *nitrum flammens*—and gives off water, nitrous acid, and nitrogen gas. According to A. Pleisch, if mixed with an equal weight of calcium chloride, and heated, nitrous acid, chlorine, and nitrogen gas are formed, then ammonium chloride sublimes, and calcium chloride mixed with some calcium oxide remains; a mixture of equal weights of ammonium nitrate and potassium chloride under similar conditions gives nitrogen, chlorine, sublimed ammonium chloride, and a mixture of potassium chloride and nitrate.

Ammonium nitrate may decompose with explosive violence when heated with reducing agents, but a strong initial impulse is usually required to start the explosion. G. Roth patented an explosive made from a mixture of *aluminium* powder and ammonium nitrate. Most of the metals are oxidized by the fused salt. J. P. Emmet [17] found that *zinc* dissolves as rapidly in the fused salt as in an acid, and evolves so much heat that the temp. of the mixture rises rapidly to 260°, when nitrogen, ammonia, and water are given off, but no nitric or nitrous oxide; *lead* also is rapidly oxidized; *antimony, bismuth, nickel, copper*, and *silver* are oxidized slowly; *arsenic, tin, iron*, and *mercury* are not affected. L. A. Buchner says that *silver* is oxidized with the evolution of nitric oxide, and the formation of ammonium silver nitrate; W. R. E. Hodgkinson and A. H. Coote say that *iron* and *aluminium* are not attacked; and that with *cadmium*, nitrogen is evolved. H. Morin studied the action of cadmium on fused ammonium nitrate, which results in the formation of a complex nitrate. According to J. P. Emmet, a fused mixture of ammonium nitrate and chloride dissolves most of the metals, including gold, platinum, rhodium, and iridium; and many metal oxides and minerals—*e.g.* titaniferous schorl, chrome iron ore, pitchblende, and molybdenum sulphide. Ammonium nitrate explodes when thrown on red-hot charcoal. R. F. Marchand found that if *phosphorus* be

projected on the fused salt, it burns brilliantly, forming phosphoric acid—if the *phosphorus* be in excess, phosphorus pentoxide is formed. J. P. Emmet found that *sulphur* can be fused with the salt without reaction.

Soln. of ammonium nitrate are reduced by many of the metals. W. R. E. Hodgkinson and A. H. Coote say that *cadmium* dissolves in the ice-cold soln. without developing any gas, and the soln. contains a nitrite, and when heated to 100° nitrogen is evolved; zinc and magnesium react slowly in consequence of the formation of a sparingly soluble double salt; *nickel* and *copper* also react very slowly; while *lead* is soon covered by a crust of lead nitrate; *aluminium, iron, silver,* and *mercury* are not perceptibly attacked. E. Ramann, however, found that *iron* reduces the soln. of ammonium nitrate: $2NH_4NO_3+Fe=Fe(NO_3)_2+2NH_3+H_2$. No hydrogen is evolved, because, said E. Ramann, it is spent in reducing the nitrate to nitrite.

Ammonium nitrate mixed with *litharge* expels ammonia from the solid salt at ordinary temp. T. J. Pelouze found that when ammonium nitrate is treated with a little *sulphuric acid*, ammonium sulphate and nitric acid are formed; the same result obtains with the dried salt in fifty times its weight of sulphuric acid provided the temp. is below 120°; but at 150°, nitrous oxide mixed with a little nitric oxide and nitric acid vapour is evolved, and sulphuric acid and water remain. If the salt be mixed with ten times its weight of sulphuric acid, about 75 per cent. of the salt forms nitric acid and ammonium sulphate, and 25 per cent. forms nitrous oxide and water. C. O. Weber reported that during the conc. of an aq. soln. of ammonium nitrate mixed with *acetic acid*, the whole mass ignites spontaneously, almost explosively, at a certain stage of the process—the reaction is a case of the ignition of hydrogen at the expense of the oxygen of the nitric acid. A little ammonium nitrate in contact with fused *potassium nitrite,* may produce incandescence, and from a similar cause. J. H. Gladstone and A. Tribe, and J. W. Gatehouse found that a cold soln. of ammonium nitrate is reduced by electrolysis, or by the *copper-zinc couple* forming ammonia; if the soln. is hot, some nitrogen peroxide is formed.

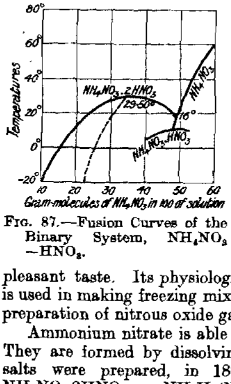

FIG. 87.—Fusion Curves of the Binary System, $NH_4NO_3-HNO_3$.

Ammonium nitrate has a sharp, bitter, unpleasant taste. Its physiological action has been studied by T. Case.[18] The salt is used in making freezing mixtures; in the manufacture of explosives; and in the preparation of nitrous oxide gas.

Ammonium nitrate is able to unite with *nitric acid* forming complex acid salts. They are formed by dissolving ammonium nitrate in nitric acid. Two of these salts were prepared, in 1879, by A. Ditte, **ammonium dihydro-trinitrate,** $NH_4NO_3.2HNO_3$, or $NH_4H_2(NO_3)_3$, which melted at 18°, and **ammonium hydrodinitrate,** $NH_4NO_3.HNO_3$, or $NH_4H(NO_3)_2$, which melted at 9°. The trinitrate prepared by E. Groschuff was in the form of prismatic needles, melting at 29·5°; the dinitrate forms thin six-sided plates, melting at 12°. A. Ditte's m.p. are lower than E. Groschuff's. R. Engel[19] showed that the solubility of ammonium nitrate in water is at first lowered by the addition of nitric acid, down to a minimum, and is then raised. The reduced solubility is supposed to be in accord with the general effect of like ions on the solubility of a salt, and this is later counterbalanced by the formation of complexes. E. Bouty studied the electrical conductivity of soln. of ammonium nitrate in nitric acid.

E. Groschuff studied the binary system $NH_4NO_3-HNO_3$ over a range of temp. −10° to 70°; and he prepared the solubility or fusion curves shown in Fig. 87. The solubility of ammonium nitrate in nitric acid is expressed in mols. of the salt in 100 mols. of nitric acid:

	8°	29·5°	16·5°	4°	11°	12°	11·5°	17°	79°
	21·1	50·0	93·5	66·7	84·3	95·1	108·0	95·1	168
	$NH_4NO_3.2HNO_3$			$NH_4NO_3.HNO_3$ (labile)				NH_4NO_3	

After passing through the eutectic minimum at 16° shown in the diagram, the curve rises to a maximum 29·5°, which represents the m.p. of the trinitrate. If the soln. be rapidly cooled to 10°, the eutectic does not appear, and by slowly cooling the liquid to 6° the dinitrate separates, and the unstable dinitrate so formed has a m.p. 12° which appears as a maximum on the curve, Fig. 87. The dinitrate, $NH_4NO_3.HNO_3$, is decomposed by water, but the solubility of ammonium trinitrate, $NH_4NO_3.2HNO_3$, has been determined. Representing the solubility in mols. of $NH_4NO_3.2HNO_3$ (as solid phase) per 100 mols. of total soln. ($NH_4NO_3.2HNO_3+H_2O$):

	−8°	−2·5°	3·0°	8·5°	19·5°	25°	29·5°
Salt	22·0	23·1	24·3	25·7	29·0	31·0	∞

The results are represented by the dotted curve, Fig. 87, which ends at 29·5°, the m.p. of the salt.

F. A. H. Schreinemakers and P. H. J. Hoenen [20] found that aq. soln. of ammonium sulphate and nitrate furnish two complex salts, **ammonium nitrato-sulphate,** $(NH_4)_2SO_4.NH_4NO_3$, and **ammonium dinitrato-sulphate,** $(NH_4)_2SO_4.2NH_4NO_3$. Both salts are decomposed by water, but are stable in the presence of an excess of ammonium nitrate.

In his memoir: *On the union of ammonia nitrate with ammonia* (1873), E. Divers [21] showed that dry ammonium nitrate absorbs considerable quantities of ammonia gas, forming a colourless, mobile liquid whose composition changes with the temp. and press. at which the absorption occurs. The change may be likened to the deliquescence of a salt in moist air. The liquefaction occurs more rapidly if the absorption occurs at 0°. The soln. has been called *Divers' liquid*, and it has the property of being able to dissolve more ammonium nitrate, and this the more the higher the temp., but the salt loses its power of absorbing ammonia as the temp. rises. F. M. Raoult measured the amount of ammonia absorbed by 100 grms. of the salt at a press. of 760 mm. and found:

	−10°	12°	18°	28°	28·5°	30·5°	40·5°	79°
Grms. NH_3 . .	42·50	33·00	31·50	23·25	21·25	17·50	6·00	0·50
	Liquid				Solid			

L. Troost believed that two definite compounds were formed, *ammonium sesquiammino-nitrate*, $2NH_4NO_3.3NH_3$, which is solid below −22°; and *ammonium triammino-nitrate*, $NH_4NO_3.3NH_3$, solid below −55°. F. M. Raoult also inclined to the view that definite compounds are formed, because the proportion of ammonia absorbed between 12° and 18° is constant 32·8 grms. per 100 grms. of the nitrate, while the amount falls from 48 grms. to 32·8 between 0° and 12°; and from 32·0 to 18·0 grms. between 18° and 30°. The ammonia absorbed in the region between 12° and 18° corresponds with L. Troost's sesqui-ammino-compound. B. Kuriloff has shown that the vapour tension rises from 90 mm. at −30° to 365 mm. at 0°, and to 930 mm. at 25°. The constancy in the vapour curve at 360 mm. corresponding with the sesqui-ammino-compound represents a sat. soln. of ammonium nitrate in ammonia. B. Kuriloff also interpreted the curves showing the composition of the product with temp. as indicated in Fig. 88. The following is a selection from the data showing the f.p. of mixtures containing the indicated number of mols. of ammonium nitrate per 100 mols. of the mixture $NH_4NO_3+NH_3$:

Grm. mol. NH_4NO_3 .	100	53·8	36·9	32·3	13·9	6·25	0°
F.p.	168°	68·8°	−10·5°	−30°	−44·5°	−60°	−80°
Solid phase	NH_4NO_3				$NH_4(NH_3)NO_3$		NH_3

It is therefore probable that in the range *AB*, Fig. 88, a sat. soln. of ammonium nitrate in liquid ammonia is involved; that the curve *BCD* covers the region of

stability of **ammonium triammino-nitrate,** $NH_4(NH_3)_3NO_3$, that the maximum *C* at about $-40°$ represents the m.p. of this compound; that the eutectic *B* lies between NH_4NO_3 and $NH_4(NH_3)_3NO_3$; and the eutectic *D*, between $NH_4(NH_3)_3NO_3$ and NH_3. The curve *DE* represents the drop in the f.p. of liquid ammonia by additions of ammonium nitrate. The dotted portions of the curves are interpolated; the circles represent observations. These results were confirmed by J. Kendall and J. G. Davidson.

Heat is liberated during the formation of Divers' liquid, the amount represents the difference in the positive latent heat of liquefaction of the ammonia, and the negative heat of soln. of the nitrate. E. Divers measured the sp. gr. of liquid and found for soln. with 49·55, 33·4, and 27·2 grms. of ammonia per 100 grms. of ammonium nitrate, at 15·5°, the numbers 1·07251, 1·1559, and 1·1996 respectively. J. F. Schröder measured the eq. conductivity between the 17·8° and 18°, and found for soln. with 12·25, 18·75, and 26·20 per cent. of ammonium nitrate, the respective conductivities $\lambda=110{\cdot}6$, 100·8, and 83·17. The conductivity is very similar to that of liquid ammonia soln. During electrolysis, E. Divers found nitrogen to be evolved at the anode, hydrogen at the cathode, in the proportion 1 : 3 by volume. The chemical properties of Divers' liquid agree with the hypothesis that it is a soln. of ammonium nitrate in liquid ammonia. E. Divers, J. Bronn and G. Arth have qualitatively noted many of these. Bromine dissolves liberating nitrogen; iodine forms a solid mass—possibly $N_2H_6I_2$. The metals potassium, sodium, cadmium, magnesium, zinc, and iron dissolve in the liquid, reducing the nitrate to nitrite—potassium inflames on the liquid as it does on water; copper and tin do not appear to be attacked. The action of phosphoric or chromic acid is not very energetic. Mercurous chloride forms metallic mercury; mercuric iodide turns white and then dissolves; potassium permanganate readily dissolves, and is then slowly decomposed; lead and platinum salts form ammino-compounds. Ether causes a separation of the liquid into ammonia and ammonium nitrate. Ammonium carbonate; lead, calcium, and silver chloride; lead iodide and nitrite; potassium nitrite; and sodium nitrate readily dissolve in the liquid, while potassium, sodium and mercuric chlorides; potassium nitrate; ammonium bromide, iodide, oxalate, and sulphate: and calcium carbonate are sparingly soluble in Divers' liquid.

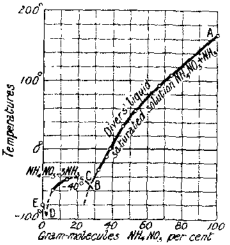

FIG. 88.—Freezing Point Curves of Mixtures of Ammonium Nitrate and Ammonia.

E. Rengade found that by adding a little water to a mixture of sodium nitrate and ammonium chloride, only the ternary mixture of solid $NaNO_3-NH_4NO_3-NH_4Cl$ can exist without change at ordinary temp.; and by adding crystals of sodium nitrate to a sat. soln. of ammonium chloride, or by shaking sodium nitrate (0·588 mol) and ammonium chloride (0·467 mol) with a little water, only the ternary mixture $NaNO_3-NH_4Cl-NaCl$ can exist under the same conditions. A. Massink studied the ternary system $(NH_4)_2SO_4-NH_4NO_3-H_2O$ at 0°, 30°, and 70°.

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§ 39. Normal or Tertiary Alkali Orthophosphates

C. G. Gmelin[1] prepared **trilithium phosphate,** Li_3PO_4, by adding a soln. of phosphoric acid to a soln. of lithium carbonate—*not the sulphate*—J. J. Berzelius used lithium acetate in place of the carbonate. C. F. Rammelsberg treated a soln. of a neutral lithium salt—chloride or acetate—with ammonium phosphate and ammonia. Unlike the other alkali phosphates the sparing solubility of lithium phosphate leads to the formation of a precipitate in all these cases. W. Mayer studied the precipitation of lithium phosphate from soln. of lithium salts with a view to the employment of the reaction for the gravimetric determination of lithium in the presence of the other alkalies. He found that when a clear soln. of a lithium salt with disodium or dipotassium hydrogen phosphate is allowed to stand, the mixture gradually becomes turbid. The precipitation occurs more readily if the soln. be neutralized with sodium or potassium phosphate mixed with ammonia, and heated. The evaporation to dryness of a mixture of a lithium salt of a volatile acid with sodium phosphate gives a residue of trilithium phosphate: $3LiNO_3 + Na_2HPO_4 \rightleftharpoons Li_3PO_4 + 2NaNO_3 + HNO_3$, from which the soluble nitrate can be removed by washing. Ammonium phosphate and ammonia can be employed in place of the sodium salt, but the lithium phosphate is more soluble in the soln. of the ammonium salt. If the free acid be neutralized with sodium carbonate, the product will be contaminated with the admixed sodium salt, but no double salt of lithium with sodium or ammonium phosphate, is formed under these conditions.

Normal or tertiary sodium phosphate appears to have been first described by T. Thomson in 1825 as a sodium phosphocarbonate. It is doubtful if the salt can exist in aq. soln., under ordinary conditions, without hydrolysis, $Na_3PO_4 + H_2O \rightleftharpoons NaOH + Na_2HPO_4$, so that an excess of sodium hydroxide is required for its preparation in the wet way. With eq. proportions of acid and base, the crop of crystals had the composition $2Na_3PO_4.Na_2HPO_4$, and the mother liquid gave feathery crystals $18Na_3PO_4.Na_2O$. According to J. H. Smith, the best way of making trisodium phosphate is to mix the mixture $36H_3PO_4 + 37Na_2CO_3$ for the first stage of the process, and mix the product with $38NaOH$. E. Mitscherlich obtained the tertiary salt by calcining disodium hydrogen phosphate with an excess of sodium carbonate; T. Graham calcined phosphoric acid, or sodium pyrophosphate, $Na_4P_2O_7$, or sodium metaphosphate with sodium hydroxide, or boiled soln. of these salts for some hours. According to G. Dragendorff, trisodium phosphate is made by passing the vapour of phosphorus over heated sodium carbonate. The anhydrous salt is most conveniently made by heating the dodecahydrate. The conc. soln., with sodium hydroxide in excess furnished hexagonal crystals of **dodecahydrated trisodium phosphate,** $Na_3PO_4.12H_2O$. C. F. Rammelsberg obtained octohedral crystals of **decahydrated trisodium phosphate,** $Na_3PO_4.10H_2O$, from the waste liquor of soda works; and J. A. Hall, and H. Baker obtained **heptahydrated trisodium phosphate** from a soln. containing equal weights of disodium hydrogen phosphate and sodium hydroxide, at about 77°. J. A. Hall could not verify C. F. Rammelsberg's decahydrate, and J. d'Ans and O. Schreiner found only the dodecahydrate as a solid phase at 25°.

T. Graham employed a similar process for **tripotassium phosphate,** K_3PO_4; a soln. of the cold mass in water furnished needle-like crystals. C. Darracq prepared what he thought to be tripotassium phosphate by fusing potassium dihydrogen phosphate, KH_2PO_4, with potassium hydroxide, but, according to L. Staudenmaier, the product is potassium metaphosphate, KPO_3.

The sodium phosphates can be made on a large scale from calcium phosphate or bone ash, the mineral phosphates, or Thomas slag. The calcium phosphate or bone ash can be digested with sulphuric acid and the resulting phosphoric acid (*q.v.*) treated with sodium carbonate or hydroxide. J. Neustadtl treated the bone ash with hydrochloric acid, and mixed the soln. with Glauber's salt, and neutralized the filtered soln. with soda. R. Holverscheit digested iron phosphate from Thomas slag with sodium sulphide under press. L. Blum,

J. T. Way, and T. Twynam heated Thomas slag with soda, and extracted the alkali phosphate with water. N. A. Hélouis and M. Rychonnet, L. Imperatori, and F. Jean calcined a mixture of the phosphate with sodium sulphate and carbon; C. Schwarz, and M. Boblique heated the mineral with iron so as to make ferric phosphate, which was then heated with sodium sulphate and carbon. In each of these cases the alkali phosphate was leached from the mass. M. Drevermann treated the iron phosphate with sodium sulphide, C. Clemm with potassium sulphide.

J. H. Smith prepared a series of crystals of the basic salt $18Na_3PO_4.Na_2O$ by crystallization from a soln. with 4 per cent. excess of sodium hydroxide. Crystals of $6Na_3PO_4.Na_2O$ were also obtained. There is nothing to show if chemical individuals, mixed crystals, or adsorption phenomena are here involved.

E. von Berg prepared colourless prismatic crystals of tetrahydrated **trirubidium phosphate,** $Rb_3PO_4.4H_2O$, by crystallization, over sulphuric acid, of a soln. of two mols. of phosphoric acid, and three of rubidium carbonate, and he obtained crystals of pentahydrated **tricæsium phosphate,** $Cs_3PO_4.5H_2O$, in a similar manner. E. G. Parker prepared trihydrated tripotassium phosphate, $K_3PO_4.3H_2O$.

According to W. Mayer, trilithium phosphate forms white pulverulent **crystals**; C. F. Rammelsberg said that the precipitated salt contained 3·23 to 7·45 per cent. of water—calculated for $2Li_3PO_4.H_2O$, 7·19 per cent.—half of which it loses at 200°; and that the salt precipitated from lithium chloride soln. in the presence of ammonia contains 11·09 per cent. of water. L. Ouvrard obtained rhombic prisms of trilithium phosphate by crystallization from molten potassium phosphate, and A. de Schulten obtained rhomboidal plates, probably hexagonal, by cooling an aq. soln. of the salt. The measurements of C. F. Rammelsberg, and H. Dufet show that the dodecahydrated trisodium phosphate, $Na_3PO_4.12H_2O$, forms trigonal crystals, and H. Steinmetz gave $a : c = 1 : 0·5394$, and $\alpha = 111° 44'$. H. Baker found crystals to be isomorphous with the corresponding arsenate, $Na_3AsO_4.12H_2O$, and vanadate, $Na_3VO_4.12H_2O$, which crystallize in the trigonal system. C. F. Rammelsberg says that decahydrated trisodium phosphate, $Na_3PO_4.10H_2O$, form octahedral crystals. The crystalline forms of the other tertiary phosphates have not been recorded.

A. de Schulten gives the **specific gravity** of trilithium phosphate as 2·41 at 15°; F. W. Clark gives 2·5111 (12°) for the sp. gr. of trisodium phosphate which has been fused; and for the ordinary anhydrous salt, 2·5367 (17·5°), H. Dufet gives 1·6445 for the dodecahydrate, and H. Schiff 1·618, and L. Playfair and J. P. Joule, 1·622 (3°). H. Schiff's values for the sp. gr. of 5, 10, 15, and 20 per cent. soln. at 15° are respectively 1·0218, 1·0445, 1·0681, and 1·0925. C. Forch found the **coefficient of expansion** of aq. soln. of tripotassium phosphate $\times 10^6$ between:

Salt per litre	0°–5°	5°–10°	10°–15°	15°–20°	20°–25°	25°–30°
106 grms.	209	243	279	310	344	365
212 grms.	326	340	356	377	394	409

F. M. Raoult found the **lowering of the freezing point** of aq. soln. of trisodium phosphate to be 0·298° per grm. in 100 grms. of water, or the mol. lowering is 48·9. G. Tammann found the **lowering of the vapour pressure** at 100° for soln. with 6·16 grms. of Na_3PO_4 per 100 grms. of water to be respectively 12·5, 31·5, and 69·8 mm., 17·47, and 45·31. According to L. Ouvrard, trilithium phosphate sinters at a red heat, but its **melting point** is much higher—T. Carnelley gives 837°. C. F. Rammelsberg says that decahydrated trisodium phosphate melts in its water of crystallization at 100°, and that it loses 48·71 per cent. of water at 110°, and the remaining 2·46 per cent. at 150°. T. Graham found dodecahydrated sodium phosphate to melt at 76·7°; T. W. Richards and J. B. Churchill give 73·3°, and they proposed this temp. as a fixed point in thermometry. J. d'Ans and O. Schreiner give 70·75° ± 0·1° for the transition point. The dodecahydrate was found by T. Graham to lose 55·19 per cent. of water at a red heat, and the remainder when re-powdered and re-calcined; while, according to C. F. Gerhardt, the salt loses 5·2 per cent., eq. to one mol. of water at 100°, and not all is lost at 200°. According to M. Amadori,

anhydrous tripotassium phosphate melts at 1340°. M. Amadori found the system $KF-K_3PO_4$ has a eutectic at 766° (20 mols. per cent. K_3PO_4), and there is a further development of heat at 700°, probably due to the decomposition of a compound. The system $KCl-K_3PO_4$ gives no indication of the formation of a definite compound. T. Graham, and M. Berthelot and W. Louguinine found the **heat of neutralization**: $2H_3PO_3aq+3K_2Oaq=36·9$ Cals., and for the sodium salt 34·03 Cals.; M. Berthelot gives 33·6 Cals. M. Berthelot and W. Louguinine give for the **heat of formation** of trisodium phosphate from its elements 452·4 Cals., and for tripotassium phosphate in aq. soln. 483·6 Cals. A. Joly gives −14·5 Cals. for the **heat of solution** of dodecahydrated trisodium phosphate in 670 mols. of water at 18° to 20°. H. Baker found the **index of refraction** of dodecahydrated trisodium phosphate for the ordinary and extraordinary rays of sodium light to be respectively 1·4486 and 1·4539; and H. Dufet found respectively 1·4458 and 1·4524. E. Doumer found the sp. optical refraction of a dil. soln. of trisodium phosphate to be 0·392, and the mol. refraction, 64·3. E. G. Parker found the crystals of anhydrous and trihydrated tripotassium phosphate to be biaxial. E. E. Brooks found that when exposed to the cathode rays lithium phosphate phosphoresces a bright light Cambridge blue.

The **electrical conductivity** of trisodium phosphate soln. has been measured by E. Bouty at 14°; by M. Berthelot at 17°; and by P. Walden at 25°. M. Berthelot finds the mol. conductivities, μ, for a mol. of the salt in v litres of water:

v	5	10	20	50	100	200	500
μNa_3PO_4	49·2	60·4	71·2	81·5	87·4	90·5	91·0
μK_3PO_4	—	74·5	85·2	97·9	105·6	107·5	108·4

With high dilutions P. Walden found the increase with dilution is very small and finally decreases, showing that the salt is completely hydrolyzed. W. Hittorf measured the **transport numbers** *of the ions of the sodium salt.*

So far as data are available the **solubilities** of the normal phosphates appear to increase in passing through the alkali family from lithium to cæsium phosphate. W. Mayer says that 100 grms. of water dissolve 0·034 grm. of trilithium phosphate at 18°, and 100 grms. of about $1·6N$-ammoniacal water 0·026 grm.; the salt is much more easily soluble in the presence of ammoniacal salts, and is precipitated by boiling such soln. with alkali hydroxides. According to W. Mayer, C. F. Rammelsberg, and A. de Schulten, trilithium phosphate is readily soluble in dil. hydrochloric, sulphuric, and even acetic acid, and barium hydroxide precipitates barium phosphate, leaving the lithium salt in soln. The solubility of trisodium phosphate in water is given by G. J. Mulder and A. B. Poggiale in grams of salt per 100 grms. of water:

	0°	10°	20°	25°	30°	40°	50°	60°	80°	100°
Grms. Na_3PO_4	1·5	4·1	11·0	15·5	20	31	43	55	81	108

The solid phase is the dodecahydrate—see Fig. 86.—O. Apfel said the solid phase between 0° and 30° is the dodecahydrate; between 30° and 50°, the decahydrate; and between 50° and 75°, probably the octohydrate. T. Graham gave 19·6 at 15·5°, and H. Schiff 10·5 at 15°. C. Darracq says tripotassium phosphate is sparingly soluble in cold water, but readily soluble in hot water. E. von Berg's tetrahydrated trirubidium phosphate is very hygroscopic and very soluble in water, likewise the pentahydrated tricæsium phosphate. H. Arctowsky found anhydrous trisodium phosphate to be insoluble in carbon disulphide.

The aq. soln. of trisodium phosphate reacts alkaline to methyl orange, phenolphthaleïn, and litmus; and neutral to Porrier's blue. The aq. soln. of trirubidium and tricæsium phosphates also react alkaline. J. Shields, J. M. van Bemmelen, and A. Kossel found that in aq. soln., trisodium phosphate is almost completely hydrolyzed by **water** into disodium hydrogen phosphate and sodium hydroxide. E. Salm calculated that the degree of hydrolysis is about 23 per cent. of the sodium or 70 per cent. of the PO_4; E. Blanc that 34·1 per cent. of a $0·012N$-soln.

is hydrolyzed at 25°. C. F. Rammelsberg obtained disodium hydrogen phosphate and sodium carbonate by recrystallizing the salt from water in air containing carbon dioxide. T. Graham found that **carbon dioxide** converts a soln. of trisodium phosphate into a mixture of disodium hydrogen phosphate and sodium carbonate, and other feeble **acids** also remove one-third the sodium. E. Filhol and J. B. Senderens found that aq. soln. of sodium phosphate when boiled with flowers of **sulphur,** react: $2S_2+3H_2O+6Na_3PO_4=2Na_2S+Na_2S_2O_3+6Na_2HPO_4$; and similarly with the potassium salt. With the sodium salt, the reaction continues until the so-called sodium sesquiphosphate is formed. B. W. Gerland says the crystalline salt, $Na_3PO_4.12H_2O$, rapidly absorbs **sulphur dioxide,** forming a syrupy liquid from which sodium hydrogen sulphite crystallizes. Alcohol precipitates oily monosodium dihydrogen phosphate from the mother liquid, and the alcohol retains the sulphite. T. Graham found that ammonia is evolved when **ammonium nitrate** is treated with trisodium phosphate; and that **silver nitrate** precipitates trisilver phosphate, Ag_3PO_4, leaving the liquid neutral. For the action of **hydrogen peroxide,** see the perphosphoric acids. According to G. Merling, trilithium orthophosphate decomposes with the evolution of ammonia when boiled with **ammonium chloride** soln., $Li_3PO_4+2NH_4Cl=LiH_2PO_4+2LiCl+2NH_3$.

E. Filhol and J. B. Senderens[2] found that if phosphoric acid be exactly neutralized with sodium hydroxide, and the soln. be evaporated in vacuo over sulphuric acid, rhomboidal prisms of trihydrated **trisodium trihydrodiphosphate,** or **sodium sesquiphosphate,** $Na_3PO_4.H_3PO_4.3H_2O$, or $Na_3H_3(PO_4)_2.3H_2O$, are formed; at 110° the crystals lose all their water of crystallization without melting, and form $Na_3PO_4.H_3PO_4$; at 200°, they lose the combined water, melt, and on cooling form an opaque enamel. E. Filhol and J. B. Senderens also obtained the pentadecahydrated sodium sesquiphosphate, $Na_3PO_4.H_3PO_4.15H_2O$, by evaporating the soln. obtained by boiling sulphur with a soln. of sodium phosphate at ordinary temp. in a stream of dry air. The crystals melt at 55° in their water of crystallization. E. Filhol and J. B. Senderens also made prismatic needles of what they regarded as a **potassium sodium sesquiphosphate,** $K_3PO_4.Na_3PO_4.2H_3PO_4.22H_2O$, but there is no evidence to show that this product is a chemical individual. Sodium *tri-, tetra- and deca-phosphates are described in connection with the corresponding* acids.

Compounds of the trialkali orthophosphates with the alkali fluorides have been prepared. Thus, H. Briegleb[3] obtained **dodecahydrated tetrasodium fluophosphate,** $Na_3PO_4.NaF.12H_2O$, by the action of soda lye on a mixture of sodium fluoride and trisodium phosphate; by melting fluorspar, tetrasodium pyrophosphate, and sodium hydroxide, and, after boiling the powdered mass with water, evaporating the aq. soln., and by boiling cryolite with trisodium phosphate and sodium hydroxide, filtering off the alumina, and evaporating for crystals. Strong boiling is to be avoided, since it is liable to decompose the compound with the separation of sodium fluoride. The octahedral crystals belong to the cubic system; their sp. gr. is 2·2165; they melt with decrepitation when heated; and 100 grms. of water dissolve 12 grms. of the salt at 25°, and 57·5 grms. at 70° forming liquids with the respective sp. gr. 1·0329 and 1·1091. A. Baumgarten used different proportions and prepared octahedral crystals of $2Na_3PO_4.NaF.(19$ and $22)H_2O$. C. F. Rammelsberg also prepared octahedral crystals of the composition $2Na_3PO_4.3NaF.36H_2O$. The system K_3PO_4-KF has a eutectic at 766°, and 20 molar per cent. of the phosphate, and there is a development of heat on the solid at 700°, due to the decomposition of a compound. R. F. Weinland and J. Alfa prepared a **potassium fluophosphate,** $P(OH)_3(OK)F$, or $H_3PO_4.KF$, by evaporating a soln. of tripotassium phosphate and potassium hydroxide in 40 per cent. hydrofluoric acid, and afterwards crystallizing the soln.; by cooling a soln. of potassium hydroxide and phosphorus pentoxide in 40 per cent. hydrofluoric acid. The crystals are monoclinic plates which, according to H. Zirngiebl, have the axial ratios $a:b:c=0·8501:1:0·6268$, and $\beta=101° 5'$. The crystals are stable in dry air, but in moist air they lose hydrogen fluoride, and

leave potassium metaphosphate. They cannot be recrystallized from water. Warm sulphuric acid leads to the evolution of hydrogen fluoride. **Rubidium fluophosphate,** $P(OH)_3(ORb)F$, and **cæsium fluophosphate,** $P(OH)_3(OCs_3)F$, were likewise prepared by R. F. Weinland and J. Alfa.

P. Chrétien prepared small prismatic crystals of **lithium iodatophosphate,** $3Li_2O.P_2O_5.18I_2O_5.11H_2O$; **sodium iodatophosphate,** $6Na_2O.P_2O_5.18I_2O_5.5H_2O$; and of **potassium iodatophosphate,** $4K_2O.P_2O_5.18I_2O_5.5H_2O$, by adding iodic acid to a syrupy soln. of monoalkalidihydrophosphide in phosphoric acid at 150°. The soln. is cooled slowly. The crystals decompose with the separation of iodic acid when digested with water. J. H. Smith prepared clusters of hair-like crystals of what he considered to be **sodium carbonato-phosphate,** $Na_3PO_4.2Na_2CO_3$, and he suggests that its constitutional formula may be:

$$(NaO)_3{\equiv}P{<}^{O}_{O}{>}C{=}(ONa)_2$$

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§ 40. Secondary Alkali Orthophosphates

In 1735, Jean Hellot [1] prepared a salt from urine, which he regarded as a kind of gypsum; F. G. Haupt described this salt in his *Diatribe chemica de sale urinæ*

perlato mirabili (Regiomont, 1740). The name *perlatum* seems to have had reference to the greasy pearl-like colour of a bead of the salt fused in the blowpipe. A. S. Marggraff examined the salt in 1745, and concluded that although it did not give off phosphorus when heated with carbon, yet it contained phosphoric acid. In 1757, J. H. Pott in his memoir on the urine salts considered it to be a kind of Glauber's salt. H. M. Rouelle, in 1776, and L. J. Proust, in 1778, showed that it contained soda. M. H. Klaproth, J. F. Westrumb, and C. W. Scheele showed that the salt is an acid sodium phosphate, but L. J. Proust thought that the contained acid was analogous with boric acid. T. O. Bergmann regarded it as containing a peculiar acid *sui generis*, derived from urine, and to which he gave the name *acidum perlatum*—perlatic acid—L. B. G. de Morveau suggested for it *acide ourétique*. The work of T. Graham showed more particularly that the salt is disodium hydrogen phosphate, Na_2HPO_4. It occurs in the urine of carnivora, and in the blood of animals. The salt was introduced as a medicine by G. Pearson in 1792, in which case it acts as a mild purgative. A. L. Lavoisier prepared potassium phosphate by neutralizing *l'alcali végétal* with phosphoric acid, much as J. Hellot prepared the sodium salt by the action of *l'alcali minéral*.

J. J. Berzelius [2] recommended making this salt by adding sodium carbonate to a boiling soln. of phosphoric acid obtained from bone ash so long as effervescence continues. The liquid is filtered if necessary in order to remove any calcium or magnesium phosphate which may be precipitated. The liquid is then evaporated for crystallization. The salt is further purified by evaporating to dryness a soln. of the salt mixed with sodium carbonate; the cold mass is leached with water, filtered, and recrystallized. E. F. Anthon says any arsenic which may be present is precipitated with the lime. In 1880, C. F. Rammelsberg found the commercial salt to contain vanadium. E. Mitscherlich and T. Graham made the salt by crystallization from a soln. of phosphoric acid and sodium carbonate or acetate. Similar processes to those used for the tertiary sodium phosphate can be employed for preparing this salt from bone ash, natural phosphates, Thomas slag, etc.

The dodecahydrate of disodium hydrophosphate, $Na_2HPO_4.12H_2O$, crystallizes from cold soln. F. J. Malaguti's analyses gave $13H_2O$, but this is a mistake, for the work of T. Clark, T. Graham, R. Fresenius, and R. F. Marchand shows that the salt contains twelve molecules of water of crystallization. T. Clark prepared the heptahydrate of disodium hydrophosphate, $Na_2HPO_4.7H_2O$, in accord with his analysis. N. A. Orloff prepared rhombohedral crystals of the dihydrate of disodium hydrophosphate by crystallization from a mixed soln. of sodium bromate and phosphate between 40° and 45°. The **dodecahydrated disodium hydrophosphate,** $Na_2HPO_4.12H_2O$, can be obtained by crystallization from aq. soln. below 36·45°; between 36·5° and 48°, **heptahydrated disodium hydrophosphate,** $Na_2HPO_4.7H_2O$; between 48° and 95·2°, **dihydrated disodium hydrophosphate,** $Na_2HPO_4.2H_2O$, is formed; and above 95·2°, the anhydrous salt is stable. H. von Blücher, and G. J. Mulder prepared anhydrous **disodium hydrophosphate,** Na_2HPO_4, by keeping the hydrated salt for many days in vacuo over conc. sulphuric acid, and T. Clark obtained it by heating the hydrated salt to 100°—at 300° sodium pyrophosphate is formed. R. F. Marchand found no evidence of a salt with a higher degree of hydration than the dodecahydrate. J. H. Smith also reported a number of acid salts, $Na_2HPO_4 : Na_3PO_4 = 17:1$; $8:1$; $6:1$; $3:1$; $3:2$; and $1:2$; but there is no evidence to show whether or not a series of mixed crystals is formed.

Anhydrous **dipotassium hydrophosphate,** K_2HPO_4, could not be obtained by T. Graham in the solid crystalline condition; L. Staudenmaier always obtained a more acid phosphate by crystallization from soln. containing eq. quantities of potassium hydroxide or carbonate and phosphoric acid. No hydrated form has been prepared. E. G. Parker, and J. d'Ans and O. Schreiner have studied the conditions under which potassium and sodium salts are formed as solid phases—*vide* Figs. 86 and 87. E. von Berg prepared **dirubidium hydrophosphate,**

Rb_2HPO_4, by the interaction of eq. quantities of rubidium hydroxide and orthophosphoric acid in conc. aqua ammonia. The resulting precipitate of ammonia rubidium phosphate loses all its combined ammonia in vacuo over sulphuric acid. E. von Berg prepared **hydrated dicæsium hydrophosphate,** $Cs_2HPO_4.H_2O$, in a similar manner.

C. F. Rammelsberg prepared a salt corresponding with $2Li_2HPO_4.Li_3PO_4$ with one and two H_2O. The conditions under which the salt is formed are vague, and its solubility is stated to be 0·5 grm. in 100 grms. of water at 15°, and it is said to lose most of its water at 150°, all at 250°, and to melt at a higher temp.

The **crystals** of heptatahydrated disodium hydrogen phosphate were found by H. Dufet [3] to be isomorphous with the corresponding arsenate. They form monoclinic prisms with axial ratios $a:b:c=1·2047:1:1·3272$, and $\beta=96°\ 57'$. He also found the crystals of the dodecahydrated salt to be monoclinic prisms with axial ratios $a:b:c=1·7319:1:1·4163$, and $\beta=121°\ 24'$. Measurements of these crystals have also been made by E. Mitscherlich, H. J. Brooke, H. Steinmetz, and C. F. Rammelsberg. H. Dufet and A. Joly have measured the rhombic bisphenoidal crystals of dihydrated disodium phosphate and found the axial ratios $a:b:c=0·9147:1:1·5687$. Soln. of dodecahydrated disodium hydrophosphate were found by C. Tomlinson, and J. M. Thomson to be readily undercooled, and when crystallization occurs, much heat is evolved, and a mass of radiating crystals is formed.

The **specific gravity** of dodecahydrated disodium hydrophosphate, $Na_2HPO_4.12H_2O$, by J. Tunnermann is 1·5139; L. Playfair and J. P. Joule 1·525 (3°); H. Kopp—*for the salt which has been fused*—1·586 (0°); H. Schiff, 1·525; H. Buignet, 1·550; H. Stolba, 1·5235 (15°); W. C. Smith, 1·535; H. Dufet, 1·5313; and J. Dewar, 1·5200 (17°). H. Dufet also found for heptahydrated disodium hydrophosphate, 1·6789; and for the dihydrate, 1·848; N. A. Orloff gives for the dihydrate, 2·066 (15°). *The sp. gr. of aq. soln. at 16°* were found by H. Schiff to be:

Per cent. $Na_2HPO_4.12H_2O$ . .	2	4	6	8	10
Sp. gr.	1·0083	1·0166	1·0250	1·0332	1·0503

H. Stolba found for a soln. sat. at 16°, 1·0511; and A. Michel and L. Krafft, at 15°, 1·0469. W. W. J. Nicol found what he called the specific **viscosity**—time of *flow of the salt soln. multiplied by 100, and divided by the time of flow of water* at 20°—to be 405·4 at 20, 291·3 at 30°, and 220·3 at 40° for a soln. nearly sat. at 30°.

J. Dewar gives 0·0000787 for the **coefficient of expansion** of solid dodecahydrated disodium hydrophosphate, and H. Kopp, between 5° and 35°, gives for *the volume v at $\theta°$ when v_1 is the volume at* 0°, $v=v_1(1+0·000830890\theta-0·0_6470990\theta^2+0·0_9179740\theta^3)$, and for the molten salt between $-37°$ and 68°, $v=v_1(1+0·000435\theta)$. C. Forch gives for a soln. of dipotassium hydrophosphate the coeff. of expansion $\times 10^6$ between:

Salt per litre .	0°–5°	5°–10°	10°–15°	15°–20°	20°–25°	25°–30°	30°–35°	35°–40°
87 grms. . .	153	196	236	272	311	244	374	404
174 grms. . .	250	277	303	331	356	376	396	416
348 grms. . .	338	349	363	379	390	405	418	432

The **melting point** of anhydrous disodium hydrophosphate is stated by T. Clark [4] to be at a red heat, when it loses 6·26 per cent. of water, and forms the pyrophosphate. He also says the pentahydrate loses 47·63 per cent. of water at 300°, and 3·47 per cent. at a red heat. C. C. Person gives the m.p. of the dodecahydrate as 34·6°, and H. Kopp 35°, when it increases 5·1 per cent. in volume on melting. T. C. Whitlock and C. E. Barfield say the water of crystallization is removed from hydrated disodium hydrophosphate by heating for one hour at 180°, while the constitutional water begins to come off at 230°, and is all expelled in one hour at 300°. H. Rose says that the water which begins to come off at 240° is simultaneously accompanied by the passage of the salt into pyrophosphate. According to D. Balareff,

disodium hydrophosphate is dehydrated at 250°+2°, even in very moist air, and this is probably the m.p. of the salt. He obtained *pT*-curves by heating the dehydrated salt with water in a glass tube of known volume. Pyrophosphate is formed under these conditions. C. C. Person gives for the **latent heat of fusion** of dodecahydrated disodium hydrophosphate, 66·8 cals. per gram, or 24,000 cals. per mol at 36·1°, and 0·454 for the **specific heat** between −20° and 2°; and 0·758 for the molten salt between 44° and 97°. The sp. ht. of the molten salt is thus greater than that of the solid salt. J. C. G. de Marignac gives for the sp. ht. of soln. in 100 and 200 mols of water (3·8 and 7·3 per cent.) between 24° and 55°, 0·9345 and 0·9617. W. Nernst and F. Koref and F. A. Lindemann give 0·323 for the heptahydrated and 0·3723 for the dodecahydrated disodium hydrophosphate. C. H. Lees found no apparent break in the **thermal conductivity** of this salt on fusion.

The **heat of formation** of disodium hydrophosphate from its elements is 413·9 Cals., according to J. Thomsen, while M. Berthelot and W. Louguinine give 414·9. With the progressive neutralization of phosphoric acid with sodium hydroxide, J. Thomsen found that 14·83 Cals. are developed with the first molecule; this rises to 27·08 Cals. with the second molecule, and to 34·03 Cals. with the third. M. Berthelot and W. Louguinine add that the first eq. of soda which combines with phosphoric acid, disengages a quantity of heat comparable with that attending the formation of the salts of strong acids. The second eq. disengages much less, scarcely more than is produced in the formation of a bicarbonate. The heat liberated by the union of the third eq. is still less, as its amount is comparable only with that set free in such reactions as the production of an alkaline phenate. But the reaction does not terminate abruptly with the third eq. of base, for the total heat continues to increase, though in a rapidly decreasing ratio, with the quantity of base added, until 5 eq. are reached. M. Berthelot found the heat of formation of dipotassium hydrophosphate in aq. soln. to be 429·2 Cals. The **heat of solution** of the dihydrate in 400 mols. of water is given by J. Thomsen as −0·4 Cal., and for the dodecahydrate, −22·8 Cals.; L. Pfaundler gives −22·9 Cals., and for the pentahydrate, 11·0 Cals., and he also gives 28·0 Cals. for the **heat of hydration** of the anhydrous salt to the dodecahydrate; J. Thomsen gives 28·47 Cals.

P. C. F. Frowein found the **dissociation pressure** of the water of crystallization in dodecahydrated disodium hydrophosphate, passing into the heptahydrate, is 4·61, 10·53, and 21·58 mm. respectively at 6·8°, 17·28°, and 27°. The calculated **heat of hydration** of this salt in this interval is 2·221 Cals.; L. Pfaundler found 2·234 Cals.; J. Thomsen, 2·244; and P. C. F. Frowein, 2·242; H. Lescœur found the dissociation press. for the heptahydrate to be 90 mm. at 20°, and for the dodecahydrate, 13·5 mm. at 20°. T. Clark found that the dodecahydrate effloresces rapidly in air between 11° and 17°, forming the heptahydrate. H. Debray, L. Pfaundler, A. Horstmann, H. H. Pareau, H. Schottky, R. E. Wilson, and H. Precht and K. Kraut have also investigated the vap. press. of this salt. For the transition 0–$2H_2O$, W. Müller-Erzbach gave 1·4 mm.; for the transition 2–$7H_2O$, H. W. Foote and S. R. Scholes gave 12·4 mm., W. Müller-Erzbach, 13·6 mm., and A. A. Noyes and L. R. Westbrook, 14·51 mm.; and for the transition 7–$12H_2O$, H. W. Foote and S. R. Scholes gave 18·0 mm. P. C. F. Frowein, 18·8 mm., H. Lescœur, 18·0 mm., W. Müller-Erzbach, 17·6 mm., and A. A. Noyes and L. R. Westbrook, 19·13 mm.

W. Müller-Erzbach says that the chemical attraction of the salt to its water of crystallization between 13° and 62° is constant. G. Tammann found the lowering of the **vapour pressure of solutions** of disodium hydrophosphate at 100° for soln. with 7·52, 34·42, and 84·12 grms. of salt per 100 grms. of water to be respectively 12·8, 49·0, and 121·0 mm. G. T. Gerlach found the **boiling point of solutions** of 8·6, 17·2, 51·4, and 110·5 grms. of disodium hydrophosphate in 100 grms. of water to be respectively 100·5°, 101°, 103°, and 106·5°. The last value probably represents a supersaturated soln. According to T. Griffiths, a sat. soln. of this same salt boils at 105°; G. J. Mulder gives 105° to 106·4°; and J. Legrand, 106·5°.

The lowering of the **freezing point of solutions** of disodium hydrophosphate has been measured by F. M. Raoult, who gives 0·260° for a gram of the anhydrous salt in 100 grms. of water; and the mol. lowering, 37·0; E. H. Loomis found for soln. with 0·01001, 0·02003, 0·05008, and 0·1002 mols. of the salt in a litre of water the respective mol. depressions 5·0°, 4·84°, 4·60°, and 4·34°. This, says E. H. Loomis, corresponds with an extensive ionization in dil. soln. $Na_2HPO_4 \rightleftharpoons 2Na^{\cdot} + HPO_4''$. According to A. Ditte, when a mixture of equal parts of ammonium nitrate and dodecahydrated disodium hydrophosphate is triturated in a mortar, the temp. drops 18°; F. Rüdorff says that 14 parts of the dodecahydrate in 100 parts of water lowers the temp. from 10·8° to 7°, and to 3·7°. H. Dufet found the **index of refraction** of dodecahydrated sodium hydrophosphate crystals to be for Na-light 1·4361; of the heptahydrate, 1·4424; and of the dihydrate, 1·4629. The optical refraction was found by E. Doumer to be 0·292, and the mol. refraction, 41·5.

The **electrical conductivity** of aq. soln. of disodium hydrophosphate has been measured by P. Walden[5] at 25°, W. Foster at 18°, E. Bouty at 14°, and M. Berthelot. The last-named found for a mol. of this salt or of dipotassium hydrophosphate in v litres of water at 17° the mol. conductivities:

v	10	20	50	100	200	500	1000	∞
μNa_2HPO_4	49·2	53·4	59·4	63·0	66·2	69·8	71·4	82·0
μK_2HPO_4	69·6	74·8	80·0	83·7	87·4	91·0	93·2	102·0

The temp. coeff. for normal soln. between 18° and 26° is 0·0236. W. Hittorf measured the **transport numbers** of the ions of the sodium salt. A. Rius y Miro found that the **electrolytic oxidation** of potassium hydrophosphate probably occurs in two stages: $K_2HPO_4 \rightarrow K_4P_2O_8 \rightarrow 2K_2HPO_5$.

The **solubility** of disodium hydrophosphate has been investigated by G. J. Mulder,[6] H. Schiff, T. Shiomi, J. d'Ans and O. Schreiner, W. A. Tilden, A. B. Poggiale, O. Apfel, A. Müller, A. Ferrein, N. Neese, and D. L. Hammick, H. K. Goadby, and H. Booth. According to G. J. Mulder, 100 grms. of water dissolve:

	0°	10°	20°	30°	40°	50°	60°	80°	100°
Grms. Na_2HPO_4	2·5	3·9	9·3	24·1	63·9	82·5	91·6	96·6	99·0
Solid phase	$Na_2HPO_4.12H_2O$				$Na_2HPO_4.7H_2O$	$Na_2HPO_4.2H_2O$			Na_2HPO_4

The solid phases were worked out by J. d'Ans and O. Schreiner; and the general results are graphed in Fig. 89. D. L. Hammick, H. K. Goadby, and H. Booth found that the dodecahydrate exists in two forms. The transition temperature of **dodecahydrate β-disodium hydrophosphate,** stable at ordinary temp., into **dodecahydrated α-disodium hydrophosphate,** is 29·6°, and this is marked by a well-defined break in the solubility curve.

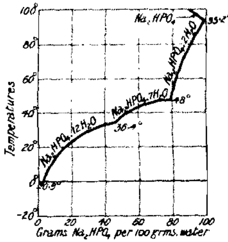

Fig. 89.—Solubility of Disodium Hydrophosphate in Water.

G. J. Mulder says that the dodecahydrate begins to melt at 35°, but is not completely liquid until over 40°, so that the true m.p. is between 40° and 41°, for between 37° and 38° the salt separates into a solid and liquid portion. For the **transition point,** $Na_2HPO_4.12H_2O \rightleftharpoons Na_2HPO_4.7H_2O + 5H_2O$, C. C. Person gave 36·4°; H. Kopp, and W. A. Tilden, 35°; A. E. Baur, 36·6° to 36·8°; A. W. C. Menzies and E. C. Humphrey, 35·2°; T. Shiomi, 36·45°; and J. d'Ans and O. Schreiner, 35·4° ± 0·05°. D. L. Hammick, H. K. Goadby, and H. Booth gave 35° for the transformation of α-$N_2HPO_4.12H_2O$ to the heptahydrate. T. Okazawa found the transition temp. is raised if sodium chloride be present. For the transition point, $Na_2HPO_4.7H_2O \rightleftharpoons Na_2HPO_4.2H_2O + 5H_2O$, T. Shiomi gives 48°; J. d'Ans and O. Schreiner, 48·35°

$\pm 0\cdot 05°$; and A. W. C. Menzies and E. C. Humphrey, 48·3°. For the transition point, $Na_2HPO_4.2H_2O \rightleftharpoons Na_2HPO_4 + 2H_2O$, T. Shiomi gives 92·5°; and A. W. C. Menzies and E. C. Humphrey, 95°. The latter also gave the cryohydric temp. −0·5°, F. Guthrie gave −0·9° for a soln. with 1·9 grms. of the anhydrous salt in 100 grms. of water. F. Rudorff gave −0·45°, and D. L. Hammick and coworkers −0·47°. The solubility of the anhydrous salt decreases as the temp. rises. E. von Berg says that dirubidium hydrophosphate, $Rb_2HPO_4.4H_2O$, is very soluble in water, and insoluble in alcohol; and the hydrated cæsium salt, $Cs_2HPO_4.H_2O$, is also very soluble in water, and the salt is not precipitated by ammonia.

J. d'Ans and O. Schreiner find that in ternary systems with variable proportions of $NaOH : H_3PO_4 : H_2O$, at 25°, the five stable solid phases are $NaOH.2H_2O$; $Na_3PO_4.12H_2O$; $Na_2HPO_4.12H_2O$; $Na_2HPO_4.7H_2O$; and $NaH_2PO_4.2H_2O$; and the range of stability of each phase is indicated in the diagram where the abscissæ represent the number of mols. of PO_4 per 1000 grms. of soln. and the ordinates the number of mols. of Na per 1000 grms. of soln. Similarly, J. d'Ans and O. Schreiner, and E. G. Parker find that with the ternary system: $KOH : H_3PO_4 : H_2O$, the five stable solid phases are $KOH.2H_2O$; $K_3PO_4.3H_2O$; K_3PO_4; KH_2PO_4; and $KH_2PO_4.H_3PO_4$. O. Apfel measured the solubility of disodium hydrophosphate in water. J. d'Ans and O. Schreiner treated likewise the ternary system,

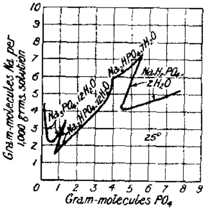

FIG. 90.—Ternary Systems, $NaOH—H_3PO_4—H_2O$.

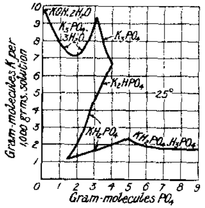

FIG. 91.—Ternary Systems, $KOH—H_3PO_4—H_2O$.

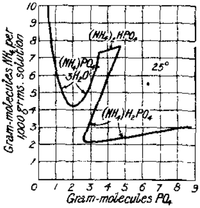

FIG. 92.—Ternary Systems, $NH_3—H_3PO_4—H_2O$.

$NH_3—H_3PO_4—H_2O$, where the three stable solid phases are $(NH_4)_3PO_4.3H_2O$; $(NH_4)_2HPO_4$; and $(NH_4)H_2PO_4$.

The aq. soln. of disodium hydrophosphate is alkaline to litmus and methyl orange, and neutral to phenolphthalein and Porrier's blue. The soln. of the potassium, rubidium and cæsium salts have an alkaline reaction. H. Friedenthal, E. Salm and J. Shields found that the **hydrolysis** of cold soln. is but small; a $\frac{1}{10}N$-soln. has $1\cdot 3 \times 10^{-9}$ mols. per litre decomposed. At ordinary temp., aq. soln. are fairly stable since the tendency of the HPO_4'' ions to pass into H_2PO_4' ions is not so great as the tendency of the PO_4''' ions to form HPO_4'' ions. E. Blanc found that 0·012N-soln. is hydrolyzed 0·066 per cent. at 25°. A. Boidin[7] found that aq. soln. of disodium hydrophosphate when heated form more or less sodium hydroxide and sodium dihydrophosphate, $Na_2HPO_4 + H_2O \rightleftharpoons NaOH + NaH_2PO_4$; the decomposition is complete at 135°.

J. S. F. Pagenstecher found that aq. soln. of disodium hydrophosphate absorb more **carbon dioxide,** and that more rapidly than is the case with water or soln. of sodium chloride; and the soln. reddens litmus more feebly than is the case with water; the carbon dioxide is not so easily removed again. J. von Liebig showed that part of the soda probably unites with the carbonic acid, and only that of dissolved gas which is uncombined follows W. Henry's pressure law. R. Heidenhain and L. Meyer found that soln. with less than one per cent. of $Na_2HPO_4.12H_2O$ absorb enough carbon dioxide to sat. the water with gas and to transform half the

soda to $NaHCO_3$ in accord with $Na_2HPO_4+CO_2+H_2=NaHCO_3+NaH_2PO_4$; as the conc. of salt increases, the proportion of hydrocarbonate formed increases more slowly than the quantity of salt in soln. With **acetic acid**, R. Fresenius found some phosphoric acid is set free; and O. Henry and E. Soubeiran, and J. W. Thomas found with strong acids, the phosphoric acid may be all liberated in a free state. R. Fresenius also found that when evaporated with **nitric or hydrochloric acid**, and heated to 150°, a mixture of disodium pyrophosphate, $Na_2H_2P_2O_7$, and sodium nitrate or chloride; if heated to a higher temp. sodium metaphosphate is formed. The **carbonates of manganese, zinc, magnesium, and the alkaline earths** were found by A. Frébault and A. Destrem to decompose disodium hydrophosphate soln., *forming acid carbonate in the cold, but the neutral carbonates if heated, and* carbon dioxide is at the same time evolved. A. Joannis found that disodium hydrophosphate absorbs gaseous or liquid **ammonia** only very slowly. H. Rose found that soln. of disodium hydrophosphate decompose **ammonium chloride.** T. Clark found that **silver nitrate** precipitates trisilver phosphate, Ag_3PO_4, from soln. of disodium hydrophosphate, and one-third the nitric acid is set free. E. Filhol and J. B. Senderens found that **sulphur** attacks soln. of disodium hydrophosphate as indicated in connection with trisodium phosphate. D. Balareff found that when heated with **thionyl chloride,** $SOCl_2$, the salt is partially dehydrated and partially converted into pyrophosphate. T. Graham found that **glass** is attacked by boiling soln., and J. H. Smith specially noted the energetic action of sodium polyphosphide on glass, **porcelain, platinum, nickel,** and **silica** vessels. The reaction is very powerful at the fusion temp. of the salt.

By neutralizing a soln. of potassium dihydrophosphate with sodium carbonate and crystallizing, E. Mitscherlich[8] obtained crystals which he regarded as **heptahydrated potassium sodium hydrophosphate,** $KNaHPO_4.7H_2O$; J. von Liebig also obtained a similar salt by adding sodium chloride to a soln. of phosphoric acid neutralized with potassium hydroxide. The monoclinic crystals are isomorphous with the corresponding sodium salt, and with the corresponding arsenates. H. Schiff says the crystals have a sp. gr. 1·671, and that they do not effloresce in air. It is not clear if a true compound or mixed crystals are here in question.

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§ 41. Primary Alkali Orthophosphates

C. G. Gmelin (1819)[1] and C. F. Rammelsberg (1849) prepared crystals of **lithium dihydrophosphate**, LiH_2PO_4, by dissolving trilithium phosphate in nitric acid, evaporating off the excess of free acid, dissolving the residue in water, and evaporating the soln. over sulphuric acid. The same salt was made by treating phosphoric acid with lithium carbonate, and evaporating the clear filtered liquid; and also by evaporating a soln. of lithium acetate in phosphoric acid. Boiling precipitated trilithium phosphate with a soln. of ammonium chloride converts it into lithium dihydrophosphate, LiH_2PO_4.

E. Mitscherlich prepared sodium dihydrophosphate, NaH_2PO_4, by adding phosphoric acid to a soln. of the disodium salt until the mixture no longer gives a precipitate with barium chloride; the soln. is conc. by evaporation, and on standing some days, crystals of monohydrated sodium dihydrophosphate, $NaH_2PO_4.H_2O$, separate out. A. Schwarzenberg added alcohol to a soln. of disodium hydrophosphate in nitric acid, and found the same salt separated out in a crystalline form while sodium nitrate remained in soln. J. J. Berzelius found that if phosphoric acid be neutralized with sodium hydroxide, disodium hydrophosphate crystallizes first from the soln., and the mother liquid furnishes crystals of sodium dihydrophosphate. He also found that if sodium hydroxide be mixed with an excess of phosphoric acid the excess may be removed by alcohol so that sodium dihydrophosphate remains. All these soln. furnish crystals of **monohydrated sodium dihydrophosphate,** $NaH_2PO_4.H_2O$. A. Joly and H. Dufet found that if a warm soln. of sp. gr. a little over 1·5 be cooled, it deposits crystals of **dihydrated sodium dihydrophosphate,** $NaH_2PO_4.2H_2O$. The same salt is produced by moistening the monohydrate. The dihydrate readily forms undercooled soln. at 20°, which always crystallize below 10°. When the crystals of the dihydrate are dried at 100° in a closed vessel, they give the monohydrate; and T. Graham found that if dried at 100°, the anhydrous salt, NaH_2PO_4, is formed. E. G. Parker, and J. d'Ans and O. Schreiner have studied the conditions under which the potassium and sodium salts are formed as solid phases—*vide* Figs. 90 to 92.

E. Mitscherlich prepared **potassium dihydrophosphate,** KH_2PO_4, by adding phosphoric acid to a soln. of potassium carbonate or dipotassium hydrophosphate until blue litmus paper is reddened and turned blue again on drying; this is evaporated until crystallization occurs. E. von Berg prepared **rubidium dihydrophosphate,** RbH_2PO_4, by evaporation of a soln. of equi-mol. parts of rubidium hydroxide and orthophosphoric acid, until crystallization begins, and finishing the evaporation over sulphuric acid; and he prepared **cæsium dihydrophosphate,** CsH_2PO_4, in a similar manner.

The preparation of these phosphates on a large scale has been the subject of investigations by T. Goldschmidt, C. V. Petraeus, H. Jay and M. Dupasquier, and Salzbergwerk Neu-Stassfurt. C. Dobrin has pointed out that great losses of potassium salts occur when primary calcium phosphate is decomposed with potassium sulphate because of the formation of a sparingly soluble double salt—calcium potassium sulphate, along with the calcium sulphate. C. Dobrin therefore recommends first converting the calcium salt into the sodium salt, and afterwards treating the sodium phosphate with potassium sulphate.

C. G. Gmelin[2] found the **crystals** of lithium dihydrophosphate are small transparent grains, whose crystalline form has not been established. The crystals of monohydrated sodium dihydrophosphate were shown by E. Mitscherlich to be dimorphous, both forms belonging to the rhombic system. E. Mitscherlich, A. Scacchi, and H. Dufet have determined the crystallographic constants. The ordinary form has the axial ratio $a:b:c=0·8170:1:0·4998$, the other has the ratio $a:b:c=0·9336:1:0·9624$. The latter are isomorphous with the corresponding salt of arsenic acid, and they appear to be formed at a rather lower temp. than the other, and they are more quickly altered by exposure to air. A. Joly and H. Dufet found dihydrated sodium dihydrophosphate to crystallize in rhombic sphenoids with the axial ratios $a:b:c=0·9147:1:1·5687$. Potassium dihydrophosphate forms tetragonal crystals which have been investigated by E. Mitscherlich, H. J. Brooke, and H. de Sénarmont. The axial ratio is $a:c=1:0·9391$. H. Baumhauer has studied the corrosion figures of the crystals. G. N. Wyrouboff says that the microscopic examination reveals the existence of two forms, so that the salt is dimorphic not monomorphic. For the isomorphism of the potassium and ammonium salts, *vide infra*. L. Staudenmaier says that the crystals grown in alkaline soln. are very short prisms; while in aq. soln. the habit is long needles. According to E. von Berg, the crystals of rubidium dihydrophosphate

are colourless four-sided prisms, and those of cæsium dihydrophosphate are in colourless plates.

According to G. Merling,[3] *the* **specific gravity** *of the crystals of lithium dihydro*phosphate is 2·461. H. Schiff gives for monohydrated sodium dihydrophosphate 2·040, and H. Dufet, 2·0547; and for the dihydrated salt, H. Dufet gives 1·9096, and A. Joly and H. Dufet, 1·915. H. Schiff gives for potassium dihydrophosphate 2·298 to 2·350; H. Buignet, 2·403; H. G. F. Schröder, 2·321 (4°); R. Krickmeyer, 2·338 (20°); *H. Topsöe and C. Christiansen*, 2·350; B. Gossner, 2·340; and W. Muthmann, 2·3325 (9·2°). F. Kohlrausch found the sp. gr. of 5, 10, and 15 per cent. soln. of potassium dihydrophosphate to be respectively 1·0341, 1·0691, and 1·1092 (water at 4° unity). C. Forch gives for the **coefficient of cubical expansion** $\times 10^6$ of aq. soln. of potassium dihydrophosphate:

Salt per litre	0°–5°	5°–10°	10°–15°	15°–20°	20°–25°	25°–30°	30°–35°	35°–40
68 grms.	95	148	197	242	283	321	358	391
136 grms.	168	208	244	283	316	344	374	404

H. Kopp gives 0·208 for the **specific heat** of potassium dihydrophosphate at 17°–18°. C. F. Rammelsberg says that lithium dihydrophosphate loses no water at 100°, but its **melting point** is rather higher and it forms on cooling a clear *transparent glass. T. Graham reported that when monohydrated sodium dihydro*phosphate is rapidly heated to 204°, the crystals melt. The salt loses its water of crystallization at 100°, and between 190° and 204° it forms disodium pyrophosphate, $Na_2H_2P_2O_7$, and it loses still more water between 204° and 244°, forming the metaphosphate. A. Joly and H. Dufet say that the dihydrated salt melts at 60°, and when heated in a closed vessel at 100°, it gives a mixture of water and crystals. W. A. Tilden found potassium dihydrophosphate melts at 96°, and if heated to a higher temp. than 204°, T. Graham found that on cooling it furnishes an opaque glass of the metaphosphate. The lowering of the f.p. of a soln. of a gram of dihydrated sodium dihydrophosphate in 100 grms. of water was found by F. M. Raoult to be 0·225°, or the mol. **lowering of the freezing point** is 27°. E. Petersen has also found that the lowering of the vap. press. of soln. of sodium dihydrophosphate in 100 grms. of water at 100° is 17·9, 57·2, and 169·9 mm. respectively; and for 13·52, 47·85, and 89·76 grms. of potassium dihydrophosphate is 19·2, 54·8, and 92·7 mm. respectively.

J. Thomsen found the **heat of neutralization** $NaOH+\frac{1}{6}H_3PO_3$=5·88 Cals.; $NaOH+\frac{1}{3}H_3PO_3$=11·34 Cals.; $NaOH+\frac{1}{2}H_3PO_3$=13·4 Cals.; $NaOH+H_3PO_4$=14·83 Cals.; and $NaOH+2H_3PO_4$=14·66 Cals.; in the latter case, M. Berthelot and W. Louguinine found 14·36. J. Thomsen also found for aq. soln. $Na_2HPO_4+\frac{1}{2}NaOH$=4·10 Cals.; Na_2HPO_4+NaOH=7·40 Cals.; and $Na_2HPO_4+2NaOH$=8·60 Cals. T. Graham found for $2H_3PO_4aq+K_2Oaq$=14·4 Cals. For the heat *of neutralization of the first molecule of orthophosphoric acid, T. Graham found* 14·4 Cals.; for the second, 9·6 Cals.; and for the third, 10·9 Cals. T. Graham found for the **heat of solution** of potassium dihydrophosphate, −4·85 Cals. S. Arrhenius gives −336 cals. for the **heat of ionization** of a $\frac{1}{10}N$-soln. at 35°.

According to H. Dufet, the **index of refraction** of solid monohydrated sodium *dihydrophosphate for Na-light is* 1·4629, and for *the* dihydrate, 1·452. H. Topsöe *and C. Christiansen give* 1·5095 *and* 1·4684 *respectively for the ordinary* and extraordinary ray of solid dipotassium dihydrophosphate. E. Doumer gives 0·200 for the optical refraction of dil. soln., 24·0 for the mol. refraction. J. H. Gladstone and W. Hibbert give for the mol. refraction of solid potassium dihydrogen phosphate, 23·69; and for the dissolved salt, 29·47. The **electrical conductivities** of soln. of sodium and potassium dihydrophosphate have been measured by M. Berthelot at 17°, E. Bouty at 14°, and P. Walden at 25°. For soln. of a mol. *of the salt in v litres of water, M. Berthelot found:*

v	10	20	50	100	200	500	1000	∞
μNaH_2PO_4	48·2	50·8	54·6	56·4	58·2	60·2	61·9	66·7
μKH_2PO_4	61·0	64·3	67·4	69·6	71·8	73·8	75·0	79·4

For the temp. coeff. of the conductivity of the sodium salt, between 18° and 52°, S. Arrhenius gives 0·0276, 0·0294, and 0·0282 respectively for 0·01, 0·1, and 0·5*N*-soln. W. Hittorf and J. F. Daniell and W. A. Miller measured the **transport numbers** of the ions of the potassium and sodium salts.

According to A. Joly and H. Dufet, the **solubility** of sodium dihydrophosphate in 100 grms. of water is 59·9 grms. of anhydrous salt at 0°, and 84·6 grms. at 18°; and T. Graham says the salt is insoluble in alcohol. O. Apfel measured the solubility of the sodium and potassium salts in water. E. Mitscherlich, L. N. Vauquelin, and H. J. Brooke say that potassium dihydrophosphate is easily soluble in water but not in alcohol; and A. Stromeyer adds that it is soluble in a 20 per cent. potassium acetate soln. E. von Berg found rubidium dihydrophosphate to be very readily soluble in water, and the salt is reprecipitated as a voluminous white crystalline powder when alcohol is added. The aq. soln. of sodium dihydrophosphate is neutral to methyl orange and acid to phenolphthalein, litmus, and Porrier's blue. Potassium dihydrophosphate reddens blue litmus paper, but the blue colour returns on drying the paper. E. Salm found the **degree of hydrolysis** of $\frac{1}{10}N$-soln. to be $3·3\times10^{-5}$ for the H·-ions. The subject has also been investigated by H. Friedenthal. The rubidium and cæsium salts also have an acid reaction. T. Graham found that a soln. of sodium dihydrophosphate gives a yellow precipitate of Ag_3PO_4 with silver nitrate and two-thirds of the nitric acid is set free. W. Foster has measured the conductivity of dil. soln. of potassium dihydrophosphate, and F. Kohlrausch the specific conductivity. A. Joannis found that dry sodium or potassium dihydrophosphate did not absorb dry **ammonia** gas; when the former salt was in contact with the liquid for 7 days at room temp. only insignificant amounts were absorbed. W. Windisch and W. Dietrich studied the action of boiling soln. of primary potassium phosphate with increasing proportions of **calcium hydrocarbonate,** and found the precipitates contained increasing proportions of tertiary calcium phosphate, with some entrained alkali.

C. F. Rammelsberg[4] evaporated a soln. of lithium phosphate in phosphoric acid in a desiccator and obtained large, transparent, deliquescent crystals, which lost no water when heated up to 150°. The analysis corresponded with **monohydrated lithium pentahydrodiphosphate,** $LiH_2PO_4.H_3PO_4.H_2O$. L. Staudenmaier evaporated equimolecular parts of sodium dihydrophosphate and orthophosphoric acid on a water-bath to a syrup, and after the liquid had stood some time, obtained crystals of **sodium pentahydrodiphosphate,** $NaH_2PO_4.H_3PO_4$. According to H. Giran, this salt is often found on the sticks of commercial metaphosphoric acid which are contaminated with sodium phosphate. E. Zettnoff considered this salt to be a pyrophosphate. **Potassium pentahydrodiphosphate,** $KH_2PO_4.H_3PO_4$, is obtained in a similar manner. The limits of stability of the potassium salt have been studied by E. G. Parker and by N. Parravano and A. Mieli—*vide* Fig. 91. L. Staudenmaier found that the potassium salt melts at 127°, the sodium salt at 131°, while N. Parravano and A. Mieli give 127·5° and 126·5° respectively. H. Giran gives for the heat of formation $H_3PO_{4solid}+NaH_2PO_{4solid}=1·44$ Cals., and for the heat of soln., 1·12 Cals. T. Salzer prepared, by chance, deliquescent crystals of **monohydrated sodium pentahydrodiphosphate,** $NaH_2PO_4.H_3PO_4.H_2O$, by evaporating a soln. of sodium trihydropyrophosphate and sodium carbonate and allowing the conc. liquid to stand for a long time.

L. Staudenmaier obtained crystals **monohydrated pentapotassium tetrahydrotriphosphate,** $2KH_2PO_4.K_3PO_4.H_2O$, by crystallization over sulphuric acid from a mixture of three mols. of potassium dihydrophosphate with one of potassium carbonate. Crystals of potassium dihydrophosphate separate first. The crystals are very soluble in water and on recrystallization give the dihydrophosphate. This salt was described by J. J. Berzelius as *Dikaliumphosphat*. L. Staudenmaier reported the formation of deliquescent crystals of another salt, **dihydrated heptapotassium pentahydrotetraphosphate,** $3K_2HPO_4.KH_2PO_4.2H_2O$, when a soln. of 50 grms. of potassium dihydrophosphate, 23 grms. of potassium hydroxide, and 50 c.c. of water, is conc. by evaporation, and allowed to stand some weeks over sulphuric acid.

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§ 42. Alkali Pyrophosphates or Diphosphates

The tetrabasicity of pyrophosphoric acid is discussed in connection with pyrophosphoric acid. Theoretically, primary, secondary, tertiary, and normal or quaternary salts should be possible according as one, two, three, or four of the acidic hydrogen atoms are replaced by basic elements. H. Giran [1] found the heats of neutralization of pyrophosphoric acid with alkali and base in aq. soln., to be $H_4P_2O_7+NaOH=NaH_3P_2O_7+15{\cdot}29$ Cals.; $H_4P_2O_7+2NaOH=Na_2H_2P_2O_7+29{\cdot}94$ Cals.; $H_4P_2O_7+3NaOH=Na_3HP_2O_7+43{\cdot}05$ Cals.; $H_4P_2O_7+4NaOH=Na_4P_2O_7+50{\cdot}91$ Cals. The heats of neutralization for successive mols. of hydrogen are therefore 15·29, 15·65, 13·11, and 7·86 Cals. Hence, H. Giran argues that pyrophosphoric acid is tetrabasic.

Tetra-alkali pyrophosphates.—C. F. Rammelsberg [2] prepared the normal lithium salt **dihydrated tetralithium pyrophosphate**, $Li_4P_2O_7.2H_2O$, by digesting soln. of lithium chloride and sodium pyrophosphate. The precipitate is dissolved in acetic acid, and reprecipitated by alcohol. G. Merling also made this salt by adding alcohol to a soln. of lithium sodium phosphate, $5Li_2O.Na_2O.3P_2O_5$.

J. J. Berzelius obtained **tetrasodium pyrophosphate**, $Na_4P_2O_7$, in 1816 by the

dehydration of ordinary sodium phosphate, $Na_2HPO_4.12H_2O$, at a red heat when the salt fuses to a transparent glass which crystallizes on cooling to a white opaque mass. T. Clark established the individuality of the salt in 1827. L. Blum also prepared this same salt by heating two mols. of sodium chloride with one of orthophosphoric acid; and F. Margueritte, by treating sodium chloride with a metallic pyrophosphate. T. Clark showed that the anhydrous salt readily dissolves in hot water, and the soln., on cooling, gives crystals of **decahydrated tetrasodium pyrophosphate,** $Na_4P_2O_7.10H_2O$; H. von Blücher found the salt loses all its water of crystallization in vacuo over sulphuric acid or even in dry air; and T. Clark, that all water is given off below red heat.

T. Graham prepared **tetrapotassium pyrophosphate,** $K_4P_2O_7$, by heating dipotassium hydrophosphate, K_2HPO_4, to redness; J. H. Gladstone, by adding phosphoric anhydride to conc. alcoholic soln. of potassium hydroxide. J. H. Gladstone also prepared this salt by adding phosphorus oxychloride gradually drop by drop to a conc. soln. of potassium hydroxide—with solid potassium hydroxide the metaphosphate is formed, and with a dil. soln., the orthophosphate is formed. The conc. of an aq. soln. of the potassium salt gives crystals of **trihydrated tetrapotassium pyrophosphate,** $K_4P_2O_7.3H_2O$. A. Schwarzenberg prepared this salt by treating an alcoholic soln. of potassium hydroxide with a slight excess of orthophosphoric acid, and afterwards adding alcohol until the liquid appears turbid. In 24 hrs. a syrupy soln. of di- and mono-orthophosphates separates. The mixture is evaporated to dryness in a platinum dish and ignited, whereby a mixture of soluble potassium pyrophosphate and insoluble metaphosphate is formed. The hydrated pyrophosphate obtained by crystallization from the soln. can be dehydrated by fusion. E. von Berg made **tetrarubidium pyrophosphate,** $Rb_4P_2O_7$, by igniting dirubidium hydrophosphate, Rb_2HPO_4; and **tetracæsium pyrophosphate,** $Cs_4P_2O_7$, was made in a similar manner.

Fused tetrasodium pyrophosphate is a white crystalline mass; the decahydrate forms monoclinic **crystals,** which were measured by C. F. Rammelsberg, W. Haidinger, A. Handl, A. Scacchi, and H. Dufet.[3] The axial ratios are $a:b:c=1.2873:1:1.8951$, and $\beta=98° 16'$. The **specific gravity** of anhydrous tetrasodium pyrophosphate is given by H. G. F. Schröder as 2·534; by H. le Chatelier, 2·3815 (17°); and by F. W. Clarke as 2·3732 (17°); for the decahydrate, L. Playfair and J. P. Joule gave 1·836; F. W. Clarke, 1·7726 (31°); H. Dufet, 1·824 and 1·8151. F. Fouqué measured the sp. gr. of soln. of the sodium salt. G. Brügelmann gives 2·33 for the sp. gr. of anhydrous tetrapotassium pyrophosphate.

G. Merling[4] found dihydrated tetralithium pyrophosphate loses 7·03 per cent. of water at 100°, and 14·55 per cent. when melted, and C. F. Rammelsberg adds that the whole of the combined water is lost when the salt melts at 200°. T. Carnelley gives the **melting point** of anhydrous tetrasodium pyrophosphate as about 880°, and H. le Chatelier gives 940°. The latter also measured the m.p. of mixtures of this compound with anhydrous borax (melting at 970°), and found a maximum in the curve at 960° and 58·3 per cent. of tetrasodium pyrophosphate corresponding with the compound $Na_4P_2O_7.3Na_2B_4O_7$, with eutectics at 910° and 850° corresponding respectively with 16·7 and 83·7 per cent. of the pyrophosphate. According to M. Amadori, tetrapotassium pyrophosphate melts at 1090°; and according to N. Parravano and G. Calcagni at 1092°; the salt also exhibits a transition point in its heating curve at 278°. M. Amadori found the system $KF-K_4P_2O_7$ has a eutectic at 730° (20 mol. per cent. $K_4P_2O_7$). The system $KCl-K_4P_2O_7$ shows no sign of the formation of a compound. H. le Chatelier obtained a eutectic at 620° with a mixture of sodium chloride with 53·4 per cent. of sodium pyrophosphate. A. Schwarzenberg found that trihydrated tetrapotassium pyrophosphate loses one-third of its water at 100°, another third at 180°, and the remaining third at 300°. E. von Berg fused both the anhydrous rubidium and cæsium salts. H. V. Regnault gives 0·22833 for the **specific heat** of the anhydrous sodium salt between 17° and 98°, and for the potassium salt, 0·19102. H. Giran gives

for the heat of formation in aq. soln., $4NaOH+H_4P_2O_7=Na_4P_2O_7+50{\cdot}91$ Cals. J. Thomsen gives 11·67 Cals. for the **heat of solution** of the anhydrous sodium salt, in 800 mols. of water, H. Giran gives 11·85 Cals., and J. Thomsen, −11·67 Cals. for the decahydrate; consequently, the **heat of hydration** of the anhydrous salt is 23·52 Cals. F. M. Raoult found the mol. **lowering of the freezing point** of aq. soln. of tetrasodium pyrophosphate is 45·8°, or 0·172° per gram of salt in 100 grms. of water. G. Tammann gives for the **lowering of the vapour pressure** of water at 100° by the soln. of 13·50, 23·99, and 33·08 grms. per 100 grms. of water, respectively 13·4, 20·7, and 27·7 mm. G. T. Gerlach found a soln. with 102 grms. of the decahydrate in 100 grms. of water boils at 101·25°. H. Dufet's value for the **index of refraction** of the anhydrous salt for the Na-line is 1·4525. E. Doumer gives 0·295 for the optical refraction, and 78·4 for the mol. optical refraction.

P. Burckhard found that the electrolysis of tetrasodium pyrophosphate is attended by the evolution of much oxygen at the anode, and at the platinum cathode, gas bubbles are formed which inflame spontaneously in air, and platinum phosphide is formed. P. Walden found the eq. **electrical conductivity** of aq. soln. of tetrasodium pyrophosphate at 25° for soln. with one gram of the salt in v litres of water:

v	32	64	128	256	512	1024
λ, $Na_4P_2O_7$	79·9	90·3	100·3	109·5	115·4	118·1
λ, Na_2HPO_4	85·1	90·7	95·6	98·5	99·8	100·7
λ, NaH_2PO_4	74·6	77·7	80·3	82·3	84·1	86·1
λ, Na_3PO_4	704·2	114·4	120·6	123·2	123·3	122·1

The conductivity of the salt $Na_4P_2O_7$ is not the same as that of Na_2HPO_4, showing, according to P. Walden, that the P_2O_7'-ions are stable in dil. soln. in agreement with the observed reactions of the salts. According to G. A. Abbott and W. C. Bray (1909), a $\frac{1}{32}N$-aq. soln. of the normal sodium salt has an electrical conductivity 31·2 units, and the $\frac{1}{1024}N$-soln. a conductivity of 53·4. By Ostwald's rule, the soln. thus appears to contain the sodium salt of a dibasic acid, probably because the salt does not retain its individuality in aq. soln. The f.p. of soln. of pyrophosphoric acid progressively neutralized by potassium hydroxide gives a curve with a well-defined minimum corresponding with $K_4P_2O_7$, with indications of $K_3HP_2O_7$, and of $K_2H_2P_2O_7$, but not of $KH_3P_2O_7$; the refractive indices of the soln., however, give a curve with a minimum corresponding with $K_2H_2P_2O_7$, and indications of $KH_3P_2O_7$. W. Hittorf measured the **transport numbers** of the ions of the sodium salt.

T. Clark [5] found tetrasodium pyrophosphate to be less readily soluble in water than the disodium hydrophosphate, Na_2HPO_4. The equilibrium conditions and transition points have not yet been worked out. According to A. B. Poggiale (1863), 100 parts of water dissolve:

	0°	10°	20°	40°	60°	80°	100°
Anhydrous salt	3·16	3·95	6·23	13·50	21·83	30·04	40·26
Decahydrate	5·41	6·81	10·92	24·97	44·07	63·40	93·11

T. Clark found that, in consequence of **hydrolysis**, soln. of tetrasodium pyrophosphate, and A. Schwarzenberg, that aq. soln. of tetrapotassium pyrophosphate, have an alkaline reaction towards litmus; E. von Berg reported that the corresponding rubidium and cæsium salts have a neutral reaction. G. von Knorre found the soln. of the sodium salt is strongly alkaline to phenolphthaleïn. A. Stromeyer found that aq. soln. of tetrasodium pyrophosphate are not converted into the orthophosphate, but that the change rapidly occurs on boiling with acetic, phosphoric, or other mineral acids, and G. Watson [6] adds that trisodium orthophosphate, disodium hydrophosphate, sodium dihydrophosphate, or orthophosphoric acid are formed according to the proportion of acid employed. A. Schwarzenberg also found that boiling with dil. potassium hydroxide converts tetrapotassium pyrophosphate into the orthophosphate, but that the change does not occur in boiling

with water alone—A. Reynoso, however, adds that water at 280° effects the conversion.

H. Struve reported that at a white heat, tetrasodium pyrophosphate is reduced by **hydrogen**, forming orthophosphate and phosphine; T. de Saussure says that when the sodium salt is heated with twice its weight of **carbon**—charcoal—phosphorus is evolved; T. Salzer, that when boiled with **bromine** water sodium bromide and hypobromite are formed; A. Jamieson, that **carbon disulphide** at a red heat forms sodium sulphide, Na_2S, and sodium metaphosphate; while H. Rose that boiling soln. with flowers of **sulphur** form orthophosphoric acid and sodium sulphite—T. Salzer found some polysulphides are formed at the same time. F. L. Winkler noted that the salt may be crystallized unchanged from soln. of **ammonium chloride**, and H. Uelsmann from soln. of **ammonia**. When calcined with ammonium chloride, A. Jamieson found that sodium chloride and metaphosphate are formed, while H. Rose found that if eight times as much ammonium salt is used, some of the phosphoric acid is volatilized as phosphorus chloride. The **metal acids** and **boric acid** form complex orthophosphates. If **hydrogen peroxide** and sodium hydrophosphate be allowed to react, a dry solid containing active oxygen eq. to 27 per cent. of H_2O_2 is formed.[7] T. Graham [8] found that **glass** is attacked by the boiling liquid.

Trialkali monohydropyrophosphates.—According to T. Salzer, if a soln. of 10 grms. of crystallized disodium hydrophosphate and 13·5 grms. of tetrasodium pyrophosphate be evaporated at a high temp. until a crust is formed, and the mother liquid be poured away, small crystals of **monohydrated trisodium hydropyrophosphate,** $Na_3HP_2O_7,H_2O$, are formed. H. Giran also prepared the salt by the action of syrupy phosphoric acid on disodium dihydropyrophosphate at 100°. The crystals are not decomposed when heated to 100°, but at 170°–190°, the water of crystallization is expelled, and at 300° the constitutional water is given off. This behaviour, said T. Salzer, is not like that of a mixture of disodium dihydropyrophosphate and tetrasodium pyrophosphate. Cold water dissolves more than one-third its weight of the salt; and silver nitrate precipitates tetrasilver pyrophosphate, $Ag_4P_2O_7$, from aq. soln. H. Giran gives for the heat of formation: $H_4P_2O_7aq + 3NaOHaq = HNa_3P_2O_7 + 3H_2O + 43·05$ Cals., and for the heat of soln. $Na_3HP_2O_7 + Aq = 6·77$ Cals. Since the heats of soln. of $Na_2H_2P_2O_7 + Aq = -2·18$ Cals., and of $Na_4P_2O_7 + Aq = 11·85$ Cals., H. Giran argues that the salt $Na_3HP_2O_7$ is not a mixture but rather a true compound. The evidence, however, is not satisfactorily demonstrative. T. Fleitmann and W. Henneberg, R. Maddrell, and H. Uelsmann regarded this salt as sodium tetraphosphate, $Na_6P_4O_{13}$. T. Salzer further found that if a small excess of the acid salt be used in the preceding preparation, a mixture of prismatic crystals of **heptahydrated trisodium hydropyrophosphate,** $Na_3HP_2O_7.7H_2O$, are formed along with a mixture of the component salts. All but one-seventh of the water is given off at 200°. C. F. Rammelsberg also claimed to have made **dihydrated trisodium hydropyrophosphate,** $Na_3HP_2O_7.2H_2O$, from the mother liquid obtained in preparing hexahydrated disodium dihydropyrophosphate. Half the water of crystallization was said to be lost at 100°, and the other half at 200°; C. F. Rammelsberg also claimed to have made crystals of $Na_3HP_2O_7.5\frac{1}{2}H_2O$, by treating tetrasodium pyrophosphate with acetic acid.

Dialkali dihydropyrophosphate.—T. Graham obtained anhydrous **disodium dihydropyrophosphate** by heating sodium dihydrophosphate, NaH_2PO_4, to between 190° and 204°; and A. Schwarzenberg, by mixing a soln. of tetrasodium pyrophosphate, $Na_4P_2O_7$, with alcohol, and afterwards washing the precipitated crystals with alcohol to remove the alkali chloride; the crystals were dried over conc. sulphuric acid. H. Dufet found the monoclinic crystals of the anhydrous sodium salt have the axial ratios $a:b:c=2·0260:1:2·0492$ and $\beta=56°\ 41'$; and the sp. gr. 1·8616. A. Schwarzenberg also prepared the corresponding **dipotassium dihydropyrophosphate,** $K_2H_2P_2O_7$, in a similar manner. K. J. Bayer obtained hexagonal prisms and plates of **hexahydrated disodium dihydropyrophosphate,** $Na_2H_2P_2O_7.6H_2O$, by crystallizing A. Schwarzenberg's salt from its aq. soln. The

salt is decomposed when heated with water. The index of refraction of the anhydrous solid sodium salt was found by H. Dufet to be 1·4645. The potassium and sodium salts dissolve in water giving aq. soln. with an acid reaction, and they are not changed to orthophosphate by boiling. The sodium salt loses 4·19 per cent. of water at 220°, and then corresponds with a *tetrasodium dihydrotetraphosphate*, $Na_4H_2P_4O_{13}$. According to C. F. Rammelsberg, the salt obtained by A. Schwarzenberg's process is **tetrahydrated disodium dihydropyrophosphate,** $Na_2H_2P_2O_7.4H_2O$, with axial ratios $a:b:c$=1·9514 : 1 : 3·3385. This salt loses its water of crystallization when dried over conc. sulphuric acid, and when melted forms glassy hexametaphosphate. If the aq. soln. be heated, the anhydrous salt separates as a pulverulent crystalline precipitate.

A. Schwarzenberg prepared fine needle-like monoclinic crystals of **dodecahydrated sodium potassium pyrophosphate,** $Na_2K_2P_2O_7.12H_2O$, by concentrating a soln. of secondary sodium pyrophosphate neutralized with potassium hydroxide. The soln. reacts alkaline. J. H. Smith prepared an impure *sodium polyphosphate*, probably $Na_4P_6O_{17}$, by evaporating mixtures of phosphoric acid with a sufficient proportion of sodium hydroxide or carbonate. The fused glassy mass dissolves slowly in cold water, more quickly in hot water. The aq. soln. is nearly neutral to methyl orange and phenolphthaleïn. It has a powerful, corrosive action on silicates and metals. Its individuality has not yet been established; it may be a congealed soln. of one or more of the other phosphates in glacial phosphoric acid.

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§ 43. Alkali Metaphosphates

As shown by T. Graham,[1] T. Fleitmann, etc., the so-called α-**sodium metaphosphate,** $NaPO_3$, is formed when sodium hydroxide is heated with an excess of phosphoric acid, and when disodium dihydropyrophosphate, $Na_2H_2P_2O_7$, or sodium dihydrophosphate, NaH_2PO_4, is heated to 315°. T. Fleitmann prepared α-**potassium metaphosphate,** KPO_3, in a similar manner. A. Jamieson prepared sodium metaphosphate by heating a mixture of tetrasodium pyrophosphate, $Na_4P_2O_7$, and ammonium chloride to redness and removing the sodium chloride by boiling dil. alcohol. R. Maddrell heated a mixture of syrupy phosphoric acid with twice its weight of sodium nitrate, and G. von Knorre gives the following details: A soln. of 20 grms. of sodium nitrate in 25 c.c. of water was mixed with 42 c.c. of orthophosphoric acid of sp. gr. 1·3, and evaporated on a water-bath. The residue was heated 4 hrs. at 330°. He found that if solid sodium nitrate be used, the nitric acid is not all expelled by this treatment. R. Maddrell and C. Darracq also prepared the potassium salt in a similar manner by using potassium chlorate in place of sodium nitrate. G. Merling made **lithium metaphosphate** by evaporating at 130° a soln. of two mols. of lithium carbonate with three of orthophosphoric acid, and the compound of ortho- and pyro-phosphate, $6Li_2O.5P_2O_5.8H_2O$, which separates is melted until the excess of metaphosphoric acid is evolved in white vapours. The product is repeatedly boiled with water and microcrystalline plates of this salt are formed. E. von Berg made **rubidium metaphosphate,** $RbPO_3$, and also **cæsium metaphosphate,** $CsPO_3$, by calcining the corresponding alkali dihydrophosphate.

The product with either the potassium sodium or lithium salt is a white powder. The lithium salt has a sp. gr. 2·461. K. Arndt and A. Gessler gave 2·144 for the sp. gr. of the sodium salt at 900°, and also of mixtures with boric oxide. T. Carnelley says the sodium salt melts at 617°; the potassium salt at 798°. M. Amadori also gave 798° for the potassium salt; N. Parravano and G. Calcagni, 823°; H. S. van Klooster, 810°. The potassium salt shows a transition point at 450°. M. Amadori found that in the binary system KF—KPO_3, there is evidence of the formation of **potassium difluometaphosphate,** $2KF.KPO_3$, at 793°; and of **potassium fluometaphosphate,** $KF.KPO_3$, at 880°, there are eutectics at 742° (20 mol. per cent. KPO_3), and at 604° (80 mol. per cent. KPO_3). There is also a break in the heating curve corresponding with a transition point in the compound $2KF.KPO_3$. The system KCl—KPO_3 exhibits no tendency to form solid soln., and the solubility is probably zero, since the transformation point of the metaphosphate is not influenced by the presence of the chloride. N. Parravano and G. Calcagni found a eutectic at 612° with a mixture of sodium metaphosphate with 69 molar per cent. of the pyrophosphate.

According to J. Thomsen, the heat of neutralization of metaphosphoric acid by soda, all in soln., is $HPO_3+\frac{1}{2}Na_2O=7·1$ Cals.; $HPO_3+Na_2O=14·38$ Cals.; $HPO_3+2NaO=16·38$ Cals.; and $HPO_3+3Na_2O=16·5$ Cals. W. Hittorf and A. Weisler measured the transport numbers of the ions of the sodium salt. K. Arndt and A. Gessler measured the conductivity of the fused salt at 900°, and also when mixed with boric oxide. T. Fleitmann and W. Henneberg say that no double salts can be made with the mono-salt, and they hence infer that it is a monometaphosphate; they also say that the sodium salt forms hexametaphosphate when melted. R. Maddrell said that potassium and sodium metaphosphates are insoluble in water, but G. von Knorre said that they are sparingly soluble. The rubidium

salt is a white powder which dissolves in water; the soln. of the rubidium salt has a neutral reaction, and that of the cæsium salt a feebly acid reaction. R. Maddrell also says the potassium salt is soluble in acids; and G. von Knorre says it dissolves with difficulty in acetic acid. According to G. Merling, the lithium salt melts at a red heat, forming a colourless, hygroscopic glassy mass which has a sp. gr. 2·226, and dissolves in water with a feeble acid reaction, and is insoluble in alcohol. T. Graham says that acids are without action on the sodium salt, and that prolonged digestion with alkali lye converts some of the salt into the orthophosphate. According to G. Tammann, if the sodium salt be allowed to stand for some weeks in contact with a soln. of potassium or ammonium chloride, the corresponding potassium or ammonium metaphosphate is formed. W. Müller says the sodium salt is not changed when heated in a stream of the vapour of carbon disulphide.

G. Tammann found that when the mother liquid remaining after the neutralization of a soln. of metaphosphoric acid with sodium carbonate, has been evaporated at 50°, crystals of what G. Tammann calls **sodium β-monometaphosphate** are obtained. These are dried on porous tiles. The salt is readily transformed into the orthophosphate. G. Tammann obtained **potassium β-metaphosphate** in a similar manner. The mol. formula is not known.

Alkali dimetaphosphates.—What T. Fleitmann called **sodium dimetaphosphate,** $(NaPO_3)_2.2H_2O$, and F. Warschauer **sodium tetrametaphosphate,** $(NaPO_3)_4.4H_2O$, was obtained by T. Fleitmann by decomposing a boiling soln. of cupric dimetaphosphate by sodium sulphide, not in excess, and evaporating for crystallization. F. Warschauer added that the finely powdered copper salt should be added in smaller portions at a time to the calculated quantity of sodium sulphide. G. Tammann used the manganese, cobalt, or zinc salts in a similar way. F. Warschauer made the same salt by neutralizing the free acid with sodium hydroxide, and removing the pyrophosphate simultaneously formed by fractional precipitation with alcohol since the pyrophosphate is more soluble in that menstruum than the metaphosphate. This salt loses its water of crystallization at 100°, and melts at a red heat; and when the molten salt is rapidly cooled, it furnishes the hexametaphosphate. The anhydrous salt is hygroscopic, and it is warmed by moistening with water. T. Fleitmann found that 100 parts of water dissolves 14 parts of the salt at ordinary temp., and but little more when warm. The soln. is neutral, and does not change after standing for a month, but with prolonged boiling, the soln. becomes more and more acid, and forms the orthophosphate. The salt dissolves readily in conc. hydrochloric acid, and separates unchanged from the soln. when alcohol is added. Orthophosphate is rapidly formed when the acid soln. is boiled. The salt separates unchanged when a soln. of the salt in sodium hydroxide lye is evaporated. The salt is insoluble in alcohol, but a little does dissolve in dil. alcohol. L. Jawein and A. Thillot found the mol. wt. by the lowering of the f.p. of aq. soln. to be 121, in agreement with the monomolecular formula, but the possibility of ionization is not taken into consideration. T. Fleitmann based the dimolecular formula on the dibasic character of the acid as evidenced by the ready formation of salts of the type $MM'P_2O_6.nH_2O$, where M and M′ are univalent radicles, and if bivalent radicles are employed corresponding compounds are formed. A. Glatzel also claims to have made about thirty double salts of this type. This evidence, however, is very weak. G. Tammann measured the electrical conductivity, the lowering of the f.p., and the temp. coeff. of aq. soln. F. Warschauer also measured the electrical conductivity and transport numbers, and concluded that the salt is really a tetrametaphosphate. Similar remarks apply to potassium dimetaphosphate, $(KPO_3)_2.2H_2O$, which F. Warschauer believes to be potassium tetrametaphosphate. The evidence, therefore, favours the hypothesis that the alleged alkali dimetaphosphates are really tetrametaphosphates. A. Holt and J. E. Myers failed to obtain the dimetaphosphates by any of the given processes, and they concluded that the so-called alkali dimetaphosphates are "probably mixtures of the alkali salts and phosphoric acids, and not definite compounds."

Alkali trimetaphosphates.—T. Fleitmann and W. Henneberg slowly heated powdered ammonium sodium hydrophosphate, $(NH_4).NaHPO_4$, to a temp. where it still showed an acid reaction, the product was then re-ground, and again heated so long as it showed a feeble acid reaction. The soluble portion was then leached from the insoluble metaphosphate, and evaporated at 30°. The resulting crystals of what T. Fleitmann and W. Henneberg regard as **sodium trimetaphosphate,** $(NaPO_3)_3.2H_2O$, was found by G. Tammann to contain still about one per cent. of an impurity which gave a voluminous precipitate with silver nitrate, calcium or barium chloride, or with zinc, manganese, nickel, or cobalt sulphate, and the precipitate is not soluble in an excess of either reagent. G. von Knorre recommended purifying the salt by treating a dil. soln. with lead nitrate, and filtering the soln. from the precipitated metaphosphate. When the filtrate is conc. by evaporation it furnishes lead trimetaphosphate. T. Fleitmann and W. Henneberg cooled molten sodium hexametaphosphate very slowly, and washed the product with not too much warm water. The liquid separated into two layers—the upper layer contained sodium trimetaphosphate, the lower layer the hexametaphosphate. C. G. Lindboom says that the last-named method of preparation is difficult, but the salt is readily made by the first-named process of T. Fleitmann and W. Henneberg; G. von Knorre, however, recommends heating a mixture of ammonium nitrate with dodecahydrated disodium hydrophosphate for 6 hrs. at 300°, and after leaching the mass with cold water, crystallizing the filtered soln. by evaporation. C. G. Lindboom also claimed to have made **potassium trimetaphosphate,** $(KPO_3)_3 3H_2O$, by heating potassium ammonium hydrophosphate, $K(NH_4)HPO_4$, several times without fusion; and also by the action of potassium sulphate on barium trimetaphosphate.

H. Kopp obtained sodium trimetaphosphate in fine triclinic rhombohedra whose sp. gr., according to F. W. Clarke, is 2·476. H. Kopp gives 0·217 for the sp. gr. between 17° and 445°. The crystals lose 24·63 per cent. of water at 100°, and on melting it loses 1·18 per cent. more water. According to A. Glatzel, the salt does not melt in its water of crystallization. A. Wiesler says that 100 parts of cold water dissolve 22·2 parts of salt; G. von Knorre adds that the soln. has a neutral reaction towards methyl orange and phenolphthaleïn, and that on boiling the soln. becomes acid and orthophosphate is produced, but the conversion is completed only when the operation is repeated a number of times. T. Fleitmann and W. Henneberg found the salt to be insoluble in alcohol and sparingly soluble in dil. alcohol. T. Fleitmann argued that the salt is a derivative of a tribasic acid from reasons analogous to those employed for the dimetaphosphates. He claims to have prepared a series of double salts of the type $M'M''P_3O_9.nH_2O$—*e.g.* $CuNaP_3O_9.3H_2O$ and $NiNaP_3O_9.4\frac{1}{2}H_2O$—another series of the type $M_3''(P_3O_9)_2.nH_2O$; and yet a third series of the type $M''M_4'(P_3O_9)_2.nH_2O$. L. Jawein and A. Thillot found a mol. wt. 103 from the lowering of the f.p. of aq. soln. This number corresponds with the mol. wt. of the simple unpolymerized acid, but the result is supposed to be invalid as evidence on account of ionization. G. Tammann's observations on the lowering of the vap. press. of aq. soln., and A. Wiesler's measurements of the electrical conductivity, lead to the same conclusion—the difference in the conductivity of soln. dil. $v=32$ and 1024 is 30·1 in agreement with W. Ostwald's rule for salts of tribasic acids. G. Tammann also measured the lowering of the f.p., the electrical conductivity and the temp. coeff. of the conductivity. A. Wiesler and W. Hittorf measured the transport numbers of the ions.

Alkali tetrametaphosphates.—T. Fleitmann prepared what he regarded as **sodium tetrametaphosphate,** $(NaPO_3)_4.4H_2O$, by treating copper, lead, cadmium, or bismuth tetrametaphosphates with sodium sulphide. Alcohol precipitates the salt from the clear soln. F. Warschauer prepared the salt by a process like that employed for the trimetaphosphate. The corresponding **lithium tetrametaphosphate,** $(LiPO_3)_4.4H_2O$, and **potassium tetrametaphosphate,** $(KPO_3)_4.4H_2O$, were made in a similar manner. The aq. soln. is neutral, and the sodium salt is obtained as a transparent hygroscopic mass by the evaporation of the aq. soln. The solid

so obtained forms elastic threads like rubber. F. Warschauer found the lithium salt loses its water of crystallization at 100°. When heated to m.p., hexametaphosphates are formed. F. Warschauer argued that this salt is a higher polymer than tetrametaphosphate, and that the electrical conductivity of its aq. soln. cannot be measured on account of dissociation. The electrical conductivity of soln. of dil. $v=32$ and 1024, give 40·6 in harmony with W. Ostwald's rule for a tetrabasic acid. Similar remarks apply to the electrical conductivities of the lithium and potassium salts. G. Tammann also measured the electrical conductivity and the temp. coeff. of aq. soln. of the sodium salt, and W. Hittorf the transport number of the ions.

Alkali hexametaphosphates.—When microcosmic salt, $(NH_4)NaHPO_4$, or sodium dihydrophosphate, NaH_2PO_4, is heated on a gradually rising temp., T. Graham found that disodium dihydropyrophosphate is first formed, and if the temp. has risen high enough to fuse the salt, a vitreous cake is obtained when the liquid is *slowly cooled*. When this product is treated with an excess of water, one portion dissolves, and the soln. furnished T. Fleitmann and W. Henneberg with sodium trimetaphosphate; the insoluble portion, called *Maddrell's salt*, is assumd to be monometaphosphate. If the molten mass be *rapidly cooled*, a vitreous, or glassy, hygroscopic mass is obtained which is easily soluble in water, and which is sometimes called *Graham's salt*. H. Rose showed that a soln. of Graham's salt furnishes precipitates partly flocculent and partly gelatinous when it is mixed with many salts of the metals or alkaline earths—*e.g.* by pouring the freshly prepared soln. into an excess of a soln. of silver nitrate, two distinct layers are formed: (i) a crystalline silver hexametaphosphate, $Ag_6P_6O_{18}$; and (ii) a gelatinous or resinous layer which is insoluble in water, and which appears to have the composition $Ag_5NaP_6O_{18}$. According to G. Tammann, Graham's salt is an impure **sodium hexametaphosphate,** $(NaPO_3)_6$, which can be purified by pouring a soln. into an excess of a soln. of silver nitrate. The crystalline precipitate is separated from the oily liquid which simultaneously separates, and transformed into the sodium salt by treatment with a soln. of sodium chloride. H. Lüdert, and G. von Knorre prepared sodium hexametaphosphate by gradually heating disodium hydropyrophosphate to redness, and rapidly cooling the fused mass.

According to T. Graham, the salt is very soluble in water, and the soln. has an acid reaction. When the soln. is evaporated at about 40° it forms a gum-like mass which, when dried over sulphuric acid, contains 9·79 per cent. of water; and if dried at 204°, it contains 7·6 per cent. of water, and consists of sodium pyrophosphate, $Na_4P_2O_7$. T. Graham says that the soln. does not change on keeping at ordinary temp., or when boiled with sodium hydroxide; but if evaporated to dryness and the residue be heated, an orthophosphate is produced. H. Lüdert adds that if the soln. be heated to say 40°, it changes into pyro- and tetraphosphate. T. Graham says the salt is soluble in alcohol, while H. Lüdert says that alcohol slowly precipitates an oily liquid from the aq. soln. L. Jawein and A. Thillot found the mol. wt. calculated from the lowering of the f.p. of aq. soln. ranged from 404 to 417. A. Weisler, and G. Tammann have measured the electrical conductivities of aq. soln.

G. Tammann (1892) inferred that Graham's salt is probably a mixture of at least three different isomeric hexametaphosphates, and this is said to be confirmed by differences in the electrical conductivities of the salts. G. Tammann assumes that the sodium is united in different ways with the anionic complex, for example, $Na_5[NaP_6O_{18}]$; $Na_4[Na_2P_6O_{18}]$; and $Na_2[Na_4P_6O_{18}]$. When ordinary sodium hexametaphosphate is digested with ammonium chloride, G. Tammann obtained sodium pentammonium hexametaphosphate, $Na(NH_4)_5P_6O_{18}$. When monopotassium dihydrogen orthophosphate is treated with silver nitrate like the corresponding sodium salt, it furnishes a mass insoluble in water, and this, when digested with silver nitrate, furnishes $K_2Ag_4P_6O_{18}.H_2O$; and when this product is treated with sodium chloride, it forms both $K_2Na_4P_6O_{18}$ and $Na_2K_4P_6O_{18}$. An analogous series

of lithium salts; $Li_2M_4P_6O_{18}$. have been prepared in which M denotes the radicle NH_4 or an atom of sodium or potassium; salts of the type $Sr_2K_2P_6O_{18}.\frac{3}{2}H_2O$ have also been made. G. Tammann (1892) found that the electrical conductivity of sodium hexametaphosphate is characteristic of a salt of a dibasic acid, and the sodium salt is accordingly symbolized: $Na_2[Na_4P_6O_{18}]$; the potassium salt, $K_2[Na_4P_6O_{18}]$, has also been made. The electrical conductivity method of finding the basicity of the acid is generally not so satisfactory because some pyrophosphate is formed when the salt is dissolved in water, presumably: $Na_6P_6O_{18}+3H_2O=3Na_2H_2P_2O_7$. The aq. soln. of sodium hexametaphosphate gives a gelatinous flocculent precipitate with barium chlorid, and this, on boiling with water, passes into barium tetrahydrogen orthophosphate, $Ba(H_2PO_4)_2$. The gum-like properties of the hexametaphosphates is characteristic. Sodium hexametaphosphate does not give precipitates with iron, nickel, copper, zinc, mercury, or lithium salts, but with manganese, magnesium, uranium, and potassium salts, precipitates are obtained which dissolve in an excess of the sodium salt; and with lead and barium salts, precipitates are obtained which do not dissolve in an excess of the sodium salt. Double salts of the general type $R_5''R_2'(P_6O_{18})_2$, where R'' represents an atom of the bivalent metal, and R' an atom of the metal of the alkalies—*e.g.* $Ca_5Na_2(P_6O_{18})_2$—are characteristic. Molten sodium hexametaphosphate resembles borax glass in dissolving metal oxides, and it or microcosmic salt is accordingly used as a blowpipe reagent.

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§ 44. Ammonium Phosphates

M. Berthelot and W. Louguinine found the heat of neutralization Q of a mol. of orthophosphoric acid by n mol. of ammonia, NH_3, all in soln., to be at 17°:

n	$\frac{1}{2}$	1	$1\frac{1}{2}$	2	5	6
Heat of neutralization .	6·71	13·46	20·32	23·14	23·33	23·70 Cals.

In dil. soln., therefore, one hydrogen of phosphoric acid is displaced by ammonium, a second very incompletely, and the third not at all. A great excess of ammonia is needed to complete the substitution of all three hydrogen atoms of phosphoric acid by ammonia. By treating aq. ammonia with phosphoric acid until the soln. reddens blue litmus, and no longer gives a precipitate with barium chloride, E. Mitscherlich [1] obtained a liquid which furnishes, when conc. by evaporation, tetragonal crystals of **ammonium dihydrophosphate,** $(NH_4)H_2PO_4$. G. von Knorre obtained this salt as an opaque white porous mass by heating diammonium hydrophosphate to 155°; according to C. F. Rammelsberg, the tetragonal crystals of the ammonium salt are isomorphous with the corresponding potassium and thallium salts, and

which, according to E. Mitscherlich, have the axial ratios $a:c=1:1{\cdot}0076$. The corresponding sodium salt is not anhydrous. A. Sabanejeff has pointed out that the salt is isomeric with primary hydroxylamine phosphite, $(NH_3O)H_3PO_3$. Mixed crystals of tetragonal potassium and ammonium dihydrophosphates have been studied by J. W. Retgers, and R. Krickmeyer. J. W. Retgers said that the two salts generally form turbid aggregates and not large clear mixed crystals, and even then, the mixed crystals occur only when the potassium or the ammonium salt is in large excess, while R. Krickmeyer could only obtain mixed crystals when the ammonium salt was in large excess—over 94·5 per cent. $NH_4H_2PO_4$—and not when the potassium salt preponderated.

The sp. gr. according to H. Schiff is 1·779; B. Gossner, 1·803; W. Muthmann, 1·794; H. G. F. Schröder gives 1·779; and R. Krickmeyer, 1·803 (19°–20°). H. Topsöe and C. Christiansen gives for the refractive indices for the ordinary ω and extraordinary ϵ rays respectively 1·5212 and 1·4768 for the *C*-line; 1·5246 and 1·4792 for the *D*-line; and 1·5314 and 1·4947 for the *E*-line. P. A. D. Berthelot gives for the mol. electrical conductivity μ, for soln. with a mol. of the salt in v litres of water:

v	10	20	50	100	200	5000	1000	∞
μ, $(NH_4)H_2PO_4$	60·0	63·3	67·0	69·0	71·4	73·6	75·2	(79·4)
μ, $(NH_4)_2HPO_4$	63·8	68·5	74·9	78·7	82·2	86·0	88·2	(98·0)
μ, $(NH_4)_3PO_4$	42·0	45·9	52·0	55·8	59·3	63·8	68·8	

The solubility of ammonium dihydrophosphate in water has been determined by O. Apfel, and G. H. Buchanan and G. B. Winner. The latter found per 100 grms. of soln.

	4·8°	18·3°	30·0°	40·0°	50·0°	69·0°	90·0°	102·0°	110·5°
Grms.	20·3	26·3	31·6	36·2	40·8	49·7	59·1	63·4	67·6

The results at $\theta°$ between 5° and 90° are represented by $S=18{\cdot}0+0{\cdot}455\theta$. The equilibrium conditions in the presence of phosphoric acid have been previously discussed, Fig. 92.

Aq. soln. of the ammonium phosphates are readily hydrolyzed. The degree of hydrolysis of ammonium dihydrophosphate in normal aq. soln., computed by A. Naumann and A. Rücker from the amounts of ammonia obtained in the distillate from aq. soln., is 0·0476; for *N*-ammonium sulphate, 0·23; for 2*N*-ammonium bromide, 0·028; and for 2*N*-ammonium chloride, 0·03. These numbers represent the percentage of free ammonia in the soln. The degree of hydrolysis increases with dilution, but except with ammonium chloride and bromide, the increase is not in accord with that computed by the formula $x^2/(1-x)=K$. Likewise for diammonium hydrophosphate, $(NH_4)_2HPO_4$, A. Naumann and A. Rücker found for 2*N*-soln., 8·0 per cent. hydrolysis; for $\frac{1}{2}N$-soln., 11·61; for $\frac{1}{4}N$-soln., 14·68; for $\frac{1}{25}N$-soln., 20·34; and for $\frac{1}{250}N$-solns., 22·43 per cent. Similarly, for triammonium phosphate, $(NH_4)_3PO_4$, the degree of hydrolysis for $\frac{3}{4}N$-soln. is 14·0 per cent.; for $\frac{3}{10}N$-soln., 17·53 per cent.; and for $\frac{3}{50}N$-soln., 25·4 per cent. C. Friedheim found that the action of a mol. of sulphuric acid on two of the ammonium dihydrophosphates is to form white prismatic crystals of a complex $NH_4H_2PO_4.(NH_4)HSO_4$. M. Berthelot has studied the distribution of barium and magnesium between phosphoric and hydrochloric acids. According to A. Joannis, dry ammonium dihydrophosphate absorbed nearly 0·5 of dry ammonia gas in 15 days. N. Parravano and A. Mieli prepared small crystalline needles of the acid salt $(NH_4)H_2PO_4.H_3PO_4$—**ammonium pentahydrodiphosphate**—by crystallization of ammonium dihydrophosphate from dil. phosphoric acid; and add that the salt can be properly dried by keeping it a long time over phosphorus pentoxide. N. Parravano and A. Mieli found the salt melts between 77° and 78°, and decomposes into $n(NH_4)H_5(PO_4)_2=(n-m)H_3PO_3+m(NH_4)H_2PO_4H_3PO_3+(n-m)(NH_4)H_2PO_4$. The salt also decomposes in contact with water.

Diammonium hydrophosphate, $(NH_4)_2HPO_4$.—T. J. Herapath,[2] and C. U. Shephard have reported the occurrence of this salt in guano; and it has been reported in the urine of carnivorous animals. E. Mitscherlich prepared crystals of the salt by the spontaneous evaporation of a mixture of phosphoric acid with an excess of ammonia or ammonium carbonate. R. Vidal noted the formation of the salt when glycol, $C_2H_4(OH)_2$, acts on phospham, NP(NH); and H. N. Stokes, during the hydrolysis of a boiling aq. soln. of monamidophosphoric acid, $NH_2.PO(OH)_2$. E. Mitscherlich and H. J. Brooke found that the crystals belong to the monoclinic *systems, and they have the axial ratios* $a:b:c=1.0143:1:1.1980$, and $\beta=91°\ 1'$. C. F. Rammelsberg says that the crystals are isomorphous with dithallous hydrogen phosphate, Tl_2HPO_4. A. Sabanejeff has pointed out that the crystals are isomeric with ammonium hydroxylamine hydrophosphite, $(NH_4)(NH_2OH)HPO_3$. The salt has a cooling, saline, pungent taste. H. Schiff's value for the sp. gr. of the salt, is 1·619; and H. Buignet's, 1·678; G. Merling found the crystals to be diamagnetic. H. Topsöe and C. Christiansen have measured the refractive indices and found for the ordinary and extraordinary rays the respective values 1·5212 and 1·4768 for the C-line; 1·5246 and 1·4792 for the *D*-line; and 1·5314 and 1·4847 for the *F*-line. E. Doumer found the optical refraction to be 0·326, and the mol. optical refraction 43·1. J. Bergengren examined the X-ray spectrum of ammonium phosphate. The electrical conductivity of aq. soln. is indicated in connection with the primary salt. J. L. M. Poiseuille measured the viscosity of the soln. in terms of the velocity of flow. The crystals effloresce on exposure to air and lose ammonia. The solubility of diammonium hydrophosphate in water has been determined by H. G. Greenish and F. A. U. Smith, who found that 100 grms. of water at 15° dissolve 131 grms. of $(NH_4)_2HPO_4$, and the sp. gr. of the soln. is 1·343. G. H. Buchanan and G. B. Winner found per 100 grms. of soln.

	0°	10°	20°	30°	40°	50	60°	70
Grms. . . .	30·0	38·4	40·7	42·5	45·0	47·1	49·3	51·5

The results at $\theta°$ between 10° and 70° are represented by $S=36.5+0.213\theta$. The equilibrium conditions in the presence of phosphoric acid have been previously discussed, Fig. 92.

When heated, the salt melts, and loses ammonia forming metaphosphoric acid—L. J. Proust obtained a 62 per cent. yield when the calculated yield is 60·6 per cent., and G. von Knorre says that the residue after heating to 350°–360° still retains much ammonia. G. von Knorre has studied the action of heat on this salt. There is the possible formation of ammonium dihydrophosphate, $(NH_4)H_2PO_4$, with a loss of 12·88 per cent.; of diammonium dihydropyrophosphate, $(NH_4)_2H_2P_2O_7$, with a loss of 19·70 per cent.; of ammonium metaphosphate, NH_4PO_3, with a loss of 26·51 per cent.; and of metaphosphoric acid, HPO_3, with a loss of 39·46 per cent. With 3–4 hrs. heating in a platinum crucible, the percentage loss of weight was:

	100°	135°	155°	166°	215°	250°	285°	350°	360°
Loss .	1·34	7·49	11·75	13·48	20·98	22·52	24·85	26·20	27·39

The crystals after heating to 100° are white and opaque, and show no signs of the formation of pyrophosphate; at 155°, the white porous mass in the upper part of the dish is largely ammonium dihydrophosphate, and the partially fused mass at the bottom of the dish contains both ortho-, pyro-, and meta-phosphoric acids—the main reactions appear to be $(NH_4)_2HPO_4=NH_3+(NH_4)H_2PO_4$; and $2(NH_4)H_2PO_4=H_2O+(NH_4)_2H_2P_2O_7$; at 166°, the residue is a viscid transparent hygroscopic mass which is mainly pyrophosphoric acid and with traces of metaphosphoric acid; at 216°, the transparent glassy mass contains pyro- and metaphosphoric acid as in the case of the product at 166°; and at 280°, a similar product is obtained, which is soluble in water, and the soln. gives an oily precipitate when alcohol is added. In no case was the formation of an insoluble metaphosphate observed. E. Mitscherlich found 100 c.c. of water dissolved 25 parts of diammonium

hydrophosphate, and the solubility of the secondary salt is rather greater than that of the primary salt. The aq. soln. were found by D. Gernez, and C. Tomlinson to be *prone to undercooling*, and E. Mitscherlich says the *soln. reacts alkaline*, and loses half its ammonia when boiled. The degree of hydrolysis of aq. soln. has been discussed in connection with the primary salt. E. Mitscherlich found the salt to be insoluble in alcohol. D. Carnegie and F. Burt found that a dil. soln. of diammonium phosphate gives a white precipitate of mercuric chloroamide, $Hg(NH_2)Cl$, when treated with a soln. of mercuric chloride; with conc. soln., dark red mercuric phosphate is precipitated which is more or less contaminated with chloride which cannot be removed by washing.

Triammonium orthophosphate, $(NH_4)_3PO_4$.—Trihydrated normal or tertiary ammonium phosphate was made by J. J. Berzelius[3] by treating a conc. soln. of diammonium hydrophosphate with conc. aq. ammonia. The magma so formed readily gives off ammonia, reforming the secondary salt. P. Schottländer prepared this salt by adding a mixture of three volumes of a 1 : 10 soln. of the secondary salt and three volumes of a 1 : 8 soln. of ammonium chloride to two volumes of aqua ammonia—sp. gr. 1·900–1·905—diluted with one volume of water, and warmed to 60°. The mixture was slowly cooled in a closed vessel. The crystals were washed with aqua ammonia and pressed between filter paper a few hours. K. Kraut and P. Schottländer find the crystals have a composition corresponding with trihydrated triammonium orthophosphate, $(NH_4)_3PO_4.3H_2O$. F. Sestini obtained a white crystalline mass of what he regarded as pentahydrated triammonium orthophosphate, $(NH_4)_3PO_4.5H_2O$, by evaporating, over quicklime, a soln. of the secondary salt in an atm. of ammonia. E. Filhol and J. B. Senderens were not able to prepare the compound $(NH_4)_3PO_4.H_3PO_4$, or $(NH_4)H_2PO_4.(NH_4)_2HPO_4$, from a soln. of phosphoric acid neutralized with ammonia. Similar remarks apply to the potassium salt, although the corresponding sodium salt was formed.

The prismatic crystals of the tertiary ammonium salt lose ammonia slowly in air, but remain unchanged in a sealed tube; they are soluble in warm water and separate out again from the cooling soln. The crystals are fairly stable in dry air, but lose two-thirds their ammonia when a soln. is boiled. The hydrolysis and electrical conductivity of aq. soln. has been discussed in connection with the primary salt. When boiled with aluminium foil, W. Smith found a feebly alkaline soln. of ammonia in phosphoric acid attacked the metal, forming a white powder; zinc, under similar conditions, gives off hydrogen and ammonia. G. Petrenko mixed a cooled soln. of triammonium orthophosphate with hydrogen peroxide and treated the mixture with alcohol. Monoclinic and rhombic crystals were obtained which in air decomposed into oxygen and ammonia. G. Petrenko represents the composition by the formula $3(NH_4O_2)_2P : O(NH_4O_2)(NH_4O)_2P : O(NH_4O_2)(NH_4O)(OH)P : O.12H_2O$; the product may be impure **ammonium perphosphate,** $(NH_4)_3PO_5$. P. Chrétien prepared **ammonium iodatophosphate,** $4(NH_4)_2O.P_2O_5.18I_2O_5.12H_2O$, analogous with the potassium salt (*q.v.*).

Sodium ammonium hydrophosphate, $NH_4NaHPO_4.4H_2O$.—This salt is also called *microcosmic salt*. T. J. Herapath found it to occur as *stercorite—stercus*, dung—in guano. In 1743, A. S. Marggraf[4] showed that the salt obtained by the evaporation of human urine contained volatile alkali and phosphoric acid; and L. J. Proust (1775) demonstrated the presence of soda in this same salt. Reference to the salt appears in the writings of the pseudo-Geber, J. I. Hollandus, J. B. van Helmont (1644), etc. From the sixteenth to the eighteenth century, this salt was called *sal urinæ fixum* to distinguish it from *sal urinæ volatile*, or ammonium carbonate; and it was also called *sal microcosmicum*, because it was derived from man, and Paracelsus supposed mankind to be an epitome, miniature, or microcosm (μικρός, small; κόσμος, world) of the exterior universe or macrocosm (μακρός, great).

J. J. Berzelius prepared crystals of **tetrahydrated sodium ammonium hydrophosphate,** $Na(NH_4)HPO_4.4H_2O$, in 1816, by cooling a hot aq. soln. of five parts secondary sodium phosphate, $Na_2HPO_4.12H_2O$, with two of the corresponding

ammonium salt; $(NH_4)_2HPO_4$. The mother liquor when further evaporated yields other crops of crystals provided the ammonia lost by evaporation be replaced. J. J. Berzelius also obtained the salt by cooling a hot soln. of six to seven parts of secondary sodium phosphate with one of ammonium chloride. G. C. Wittstein showed that products need to be recrystallized in order to eliminate contaminating sodium chloride. If the sodium phosphate used has hydrophosphate as impurity, F. L. Winkler says the latter crystallizes out alone, while the former produces the double salt.

J. L. Proust says the crystals have a saline and somewhat ammoniacal taste. The crystals of microcosmic salt are formed in large, transparent, colourless prisms belonging to the monoclinic system, and, according to E. Mitscherlich, they have the axial ratios $a:b:c=2.8826:1:1.8616$, and $\beta=99°\ 18'$. H. Schiff gives the sp. gr. 1·554, while T. J. Herapath gave 1·6159 for stercorite with 9 per cent. impurity. When heated, the crystals effloresce and give off ammonia when exposed to the air. T. Graham says that the crystals melt very easily when heated, and lose ammonia and water, leaving a residue of sodium dihydrophosphate, NaH_2PO_4, and, adds E. Mitscherlich, all the combined water is given off at a higher temp., and the salt is converted into a transparent glass—sodium hexametaphosphate—which is used as a flux for metallic oxides. G. von Knorre places the m.p. at 79°, and he says that after three hours' heating at 100°, it loses only 0·6 per cent. of ammonia; at 200°, it forms disodium dihydrophosphate, $Na_2H_2P_2O_7$; the formation of soluble trimetaphosphate begins about 240°, and of insoluble metaphosphate at about 245°; at 280° a considerable proportion of sodium metaphosphate is formed; and the remaining ammonia is slowly lost at about 310°. More particularly, three mols. of water are expelled below 62°, a fourth below 160°; and a fifth along with ammonia is not completely expelled at 360°. It is thought that the three molecules of water expelled below 100° are united in the molecule as bivalent H_2O-groups (oxygen quadrivalent), and that the others are in the hydroxylic form. These hypotheses give the graphic formula :—

$$\begin{array}{l} NaO \\ NH_4O \end{array}\!\!>P-\begin{array}{l} HO=OH_2 \\ HO=OH_2 \\ HO=OH_2 \end{array}$$

The salt is very soluble in water—100 grms. of cold water dissolve 16·7 parts of the salt, and 100 parts of hot water dissolve 100 parts of salt—the soln. loses ammonia when heated. J. M. Thomson and W. P. Bloxam found that the supersaturated soln. crystallizes when seeded with a crystal of the solid salt—this is taken as showing the existence of the undissociated solid in the soln. J. M. van Bemmelen found that but very little ammonia can be separated by dialysis. J. Thomsen gives -10.8 Cals. for the heat of soln. of a mol. of the salt in 800 mols. of water at 18°. E. Doumer gives 0·303 for the optical refraction of the salt in dil. soln., and 45 for the mol. refraction.

According to H. Uelsmann, if a hot soln. of microcosmic salt in conc. aqua ammonia be cooled, crystals of hexahydrated **sodium pentammonium diphosphate,** $(NH_4)_5Na(PO_4)_2.6H_2O$, are formed, which, on calcination, give a mixture of sodium metaphosphate and metaphosphoric acid. Again, H. Uelsmann found that if cold conc. soln. be used, crystalline plates of **sodium diammonium phosphate,** $(NH_4)_2NaPO_4.4$(or 5)H_2O, separate out. The crystals are washed with aqua ammonia. On exposure to air, or on evaporating the aq. soln., ammonia is given off, and microcosmic salt is formed. A. Herzfeld and G. Feuerlein prepared crystals of **disodium ammonium phosphate,** $Na_2(NH_4)PO_4.12H_2O$, by the action of ammonia gas on a conc. soln. of disodium hydrophosphate. H. Uelsmann claims to have made **pentahydrated sodium ammonium hydrophosphate,** $(NH_4)NaHPO_4.5H_2O$, by the spontaneous evaporation of the mother liquid remaining after the preparation of sodium pentammonium diphosphate, $(NH_4)_5Na(PO_4)_2.6H_2O$. A. Schwarzenberg did not succeed in making a **potassium ammonium orthophosphate**—*potassium microcosmic salt*—either from a mixture of dipotassium hydrophosphate and ammonium chloride, or by saturating a soln. of potassium dihydrophosphate with ammonia, and spontaneously evaporating the soln. S. S. Sadtler prepared the mixed salt from phosphorite. P. W. Bridgman represented a commercial preparation by $(NH_4)_2KPO_4.4H_2O$. The salt becomes

anhydrous by heating in vacuo for 2 hrs. at 100°. He found evidence of a transition point near 100° at 11,480 kgrms. per sq. cm., or at 86°, and 11,800 kgrms. press.; but none at room temp. up to 120,000 kgrms. per sq. cm. press. There is another transition at 128°. It is assumed that there are three modifications of this salt; but that the substance itself is unstable and gradually changes to some other substance with a change in volume. The fact that the change in volume is a decrease shows that the unstability is the result of high press. and not by a high temp. The change is not accompanied by an alteration in the colour, or by the evolution of ammonia. J. J. Berzelius reported the formation of **lithium ammonium hydrophosphate**—*lithium microcosmic salt*—analogous to the corresponding sodium salt, by evaporating a soln. of a lithium salt with diammonium hydrophosphate; but W. Meyer and C. F. Rammelsberg obtained only trilithium orthophosphate, Li_3PO_4, under these conditions.

E. Filhol and J. B. Senderens claim to have made **sodium ammonium sesquiphosphate,** $Na_3PO_4.(NH_4)_3PO_4.2H_3PO_4.3H_2O$, analogous to the sodium salt (*q.v.*). This compound—if it be a compound—is said to be very unstable and readily decomposed by water into an acid and a basic salt.

Ammonium pyrophosphates.—A. Schwarzenberg [5] prepared normal or quaternary ammonium pyrophosphate by adding alcohol to a sat. soln. of pyrophosphoric acid in aqua ammonia. He found that small crystals of tetrammonium pyrophosphate, $(NH_4)_4P_2O_7$, separated when the mixture was allowed to stand for 24 hrs. The salt is very soluble in water, and reacts alkaline. When the aq. soln. is heated with ammonia, it forms triammonium orthophosphate, $(NH_4)_3PO_4$; and if the aq. soln. be boiled alone, it forms **diammonium dihydropyrophosphate,** $(NH_4)_2H_2P_2O_7$. A. Schwarzenberg prepared secondary ammonium pyrophosphate by dissolving normal ammonium pyrophosphate in acetic acid, and mixing the soln. with alcohol, until the syrupy liquid which separates crystallizes. The crystals are freed from acetic acid by washing with water. G. von Knorre made the same salt by heating diammonium hydrophosphate, $(NH_4)_2HPO_4$, in a platinum dish at 155°. The salt is readily soluble in water, the soln. reacts acid, and it can be boiled without forming orthophosphate.

A. Schwarzenberg made monoclinic prisms of **disodium diammonium pyrophosphate,** $Na_2(NH_4)_2P_2O_7$, by evaporating a mixture of secondary sodium pyrophosphate and aqua ammonia over quicklime and ammonium chloride. The crystals are readily soluble in water, and the soln., when boiled, loses ammonia. A. Schwarzenberg prepared crystals of **hemihydrated dipotassium ammonium hydropyrophosphate,** $K_2(NH_4)HP_2O_7.\frac{1}{2}H_2O$.

Ammonium metaphosphates.—The product obtained by H. N. Stokes [6] by boiling monamidophosphoric acid, $NH_2.PO(OH)_2$, is either **ammonium monometaphosphate,** or a mixture of different metaphosphates—*vide infra*. G. Tammann prepared microscopic crystals of what he called **ammonium β-monometaphosphate,** NH_4PO_3, by crystallization in the cold of a soln. of phosphorus pentoxide and glassy metaphosphoric acid with ammonium carbonate. A soln. of the purified salt gives a white precipitate with silver nitrate. The air-dried salt has the composition $NH_4PO_3.3{\cdot}4H_2O$; and it passes in a few weeks into the orthophosphate.

Ammonium dimetaphosphate, $(NH_4)_2P_2O_6$.—T. Fleitmann prepared the anhydrous salt by treating copper dimetaphosphate with a soln. of ammonium sulphide in aqua ammonia. The filtered soln. is then treated with alcohol. C. G. Lindboom, and A. Sabanejeff prepared the same salt by melting sodium dihydrophosphate, and purifying the product by crystallization; the sodium dimetaphosphate so obtained was transformed into the barium salt, and the latter treated with ammonium sulphate. A. Glatzel obtained **tetrahydrated ammonium dimetaphosphate,** $(NH_4)_2P_2O_6.4H_2O$, by crystallization from very conc. soln.

The crystals of the anhydrous salt are short prisms belonging to the monoclinic system. T. Fleitmann found that 100 parts of cold or hot water dissolve 87 parts of the salt. A. Glatzel found that the salt is easily soluble in acids, and when the acidified soln. are boiled orthophosphoric acid is formed. The aq. soln. has an alkaline reaction, and when boiled it becomes acid, and contains no more

metaphosphate. L. Jawein and A. Thillot calculated the mol. wt. 118 from the lowering of the f.p. of aq. soln.—the value calculated for $(NH_4)_2P_2O_6$ is 97. G. Tammann, and A. Sabanejeff, have measured the lowering of the f.p., the electrical conductivity, and the temp. coeff. of aq. soln. T. Fleitmann found that when the anhydrous salt is heated to 200°–250°, it forms insoluble monometaphosphate, NH_4PO_4, which does not change at 300°, but melts with the loss of ammonia at a red heat. A. Glatzel says that when the tetrahydrate is heated to 200°, it loses its water of crystallization, and a large portion of the product is insoluble in water. The insoluble fraction is thought to be T. Fleitmann's monometaphosphate, the soluble portion is ordinary ammonium phosphate. If the hydrated salt be suddenly heated, it swells and bloats with the evolution of ammonia, and finally melts to a clear glassy metaphosphoric acid.

T. Fleitmann prepared what he regarded as **hydrated sodium ammonium dimetaphosphate,** $Na(NH_4)P_2O_6.H_2O$, by evaporating in air, or adding alcohol to a mixed soln. of the component salts. The crystals lose their water of crystallization at 110°. They are more soluble in water than the sodium salt, and less soluble than the ammonium salt. T. Fleitmann also prepared **potassium ammonium dimetaphosphate,** $2K_2P_2O_6.5(NH_4)_2P_2O_6$, by crystallization from a mixed soln. of the component salts in the respective mol. proportion 1 : 3 ; with equi-molecular proportions, the salt, $3K_2P_2O_6.(NH_4)_2P_2O_6.4H_2O$, is obtained.

Ammonium trimetaphosphate, $(NH_4)_3P_3O_9$. C. G. Lindboom, and G. von Knorre made this salt and also the double salt, **ammonium barium trimetaphosphate,** $NH_4BaP_3O_9.H_2O$. G. Tammann's **lithium diammonium trimetaphosphate,** $Li(NH_4)_2P_3O_9.4H_2O$, possibly belongs to this class of compounds. The last-named compound was made by allowing insoluble lithium metaphosphate to stand for a week in contact with a soln. of ammonium chloride. It is not perceptibly soluble in cold water, but dissolves copiously at 70°, forming an acid liquid from which the salt does not separate on cooling. G. Tammann measured the electrical conductivities of the soln.

Ammonium tetrametaphosphate.—F. Warschauer prepared **ammonium tetrametaphosphate,** $(NH_4)_4P_4O_{12}$, by the action of a soln. of ammonium sulphide in aqua ammonia upon copper tetrametaphosphate. The filtered soln. is either treated with alcohol or allowed to evaporate spontaneously. Fine crystals can be obtained by the recrystallization of the aq. soln. If a trace of ammonium sulphide be retained by the salt as impurity, the crystals become yellow when exposed to light. The crystals were found by W. Müller to be tetragonal with axial ratios $a : c = 1 : 1.1799$. The salt is more readily soluble in water than the corresponding sodium or potassium salts ; according to A. Glatzel, 100 parts of water dissolve 12·5 parts of the salt, and the soln. has a feeble acid reaction. A. Glatzel says that when the aq. soln. is evaporated in air, it forms a viscid mass from which **tetrahydrated ammonium tetrametaphosphate,** $(NH_4)_4P_4O_{12}.4H_2O$, separates at 30°. The hydrate loses water at 150°, and becomes almost insoluble and no longer behaves as a tetrametaphosphate. The ammonia is driven off at a red heat and some of the acid is simultaneously volatilized. When the aq. soln. is boiled with acids, an orthophosphate is formed. F. Warschauer measured the electrical conductivities of aq. soln.

Ammonium pentametaphosphate.—G. Tammann (1892) claims to have made ammonium pentametaphosphate, $(NH_4)_5P_5O_{15}$, by heating ammonium dimetaphosphate at 200°–250°, and treating the resulting mass with water. The same salt is made by dissolving ammonium decametaphosphate in hot water ; alcohol precipitates the salt from this soln. in white amorphous masses which have not been obtained in the crystalline state, but if the soln. be evaporated on a clock glass a stellate film is formed. G. Tammann measured the electrical conductivities of the soln. When this salt is treated with potassium bromide, **ammonium tetrapotassium pentametaphosphate,** $K_4(NH_4)P_5O_{15}.6H_2O$, separates from the soln. ; similarly, sodium or lithium chloride gives an analogous **ammonium tetrasodium**

pentametaphosphate, $Na_4(NH_4)P_5O_{15}$, or **ammonium tetralithium pentametaphosphate,** $Li_4(NH_4)P_5O_{15}$. G. Tammann has measured the electrical conductivities of soln. of lithium and sodium salts. The potassium salt furnishes a crystalline mass, the others form gum-like masses on evaporating the aq. soln. There are several other differences between the potassium and ammonium salts—$K_4(NH_4)P_5O_{15}$ and $(NH_4)_4(NH_4)P_5O_{15}$—and the sodium and lithium salts—$Na_4(NH_4)P_5O_{15}$ and $Li_4(NH_4)P_5O_{15}$. For instance, the behaviour of the two series of salts towards reagents is not quite the same; and the electrical conductivity of the potassium salt agrees with the assumption that it furnishes five cations, while the other salts furnish one cation and thus behave like salts of a monobasic acid; and it is therefore inferred that $[M_4P_5O_{15}]$ behaves as a monobasic complex ion, an inference which is confirmed by the substitutions just indicated. By treating the ammonium salt with silver nitrate, a pulverulent salt with the empirical composition $AgPO_3.\frac{1}{2}H_2O$ is obtained. When this is treated with the ammonium salt, it furnishes a crystalline product, $Ag_4(NH_4)P_5O_{15}.2H_2O$. Soln. of the sodium and lithium salts (1) give no precipitate with mercuric or cadmium chlorides, or with cupric sulphate—although the ammonium salt does give a gum-like mass; (2) with barium or ferric chloride and lead nitrate, precipitates are formed which are insoluble in an excess of reagent; (3) strontium chloride, or bismuth, or silver nitrate gives a flocculent precipitate soluble in an excess of reagent; and (4) calcium chloride, or nickel, cobalt, manganese, zinc, ferrous, or aluminium sulphate gives a gum-like separation or a flocculent precipitate. The solubilities of these precipitates in an excess of their components indicates the formation of complex salts.

Ammonium decametaphosphate.—G. Tammann prepared what he called **ammonium decametaphosphate,** $(NH_4)_{10}P_{10}O_{30}$, by heating ammonium dimetaphosphate between 200° and 250° for 2 or 3 hrs. An intramolecular change occurs and the opaque mass has an acid reaction. If the heating be protracted too long, or if maintained at too high a temp., a viscid liquid is formed. The salt is insoluble in water at 20°, but if 100 grms. of water be allowed to stand for two months in contact with the solid 1·20 and 1·54 grms. pass into soln. Hot water dissolves the product rapidly, and there is no separation on cooling, so that the decametaphosphate undergoes a transformation—the pentametaphosphate is formed. G. Tammann also found that if R. Maddrell's insoluble salt is allowed to stand 12 weeks, or the second insoluble sodium metaphosphate is allowed to stand 8 weeks, in contact with a soln. of ammonium chloride, **dodecahydrated ammonium decametaphosphate,** $(NH_4)_{10}P_{10}O_{30}.12H_2O$, is formed in irregular shaped particles. Ammonium decametaphosphate is partly changed by treatment with soln. of the metal salts—*e.g.* potassium hydroxide, or potassium chloride gives **ammonium enneapotassium decametaphosphate,** $K_9(NH_4)P_1\ O_3.10H_2O$, as an insoluble crystalline powder. When the deca-salt is treated with hot water, two mol. eq. of pentametaphosphate are obtained.

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§ 45. The Relations between the Alkali Metals

The five elements, lithium, sodium, potassium, rubidium, and cæsium, called the alkali metals, exhibit an interesting gradation in the properties of the elements and their compounds in accord with the increase in their atomic weights, from member to member, in passing from lithium to cæsium. The metals are silvery white, soft enough to be cut with a knife, rapidly tarnish in air, and decompose water at ordinary temperatures. The lowest temperature at which the action of the different metals on water can be detected is −98° for sodium, −105° for potassium, −108° for rubidium, and −116° for cæsium. The elements are all univalent, and manifest a remarkable affinity for oxygen ; cæsium and rubidium ignite spontaneously if placed in dry oxygen at the room temperature. Sodium and lithium, though compatible with the other members of the family, have feebler affinities. The chemical activity of the alkali metals appears to increase steadily in passing from lithium to cæsium. The gradation in the physical properties is illustrated in Table LXIV.

The elements have remarkably low specific gravity, and a high atomic volume (*q.v.*). The oxides and hydroxides are markedly basic ; they do not exhibit acidic qualities. The physical properties of the salts—solubility in water, molecular volume, optical properties, and the variation in the form of the crystals show the same order of variation as the atomic weights of the elements. Lithium differs in many respects from the other members of the family. The salts of the alkali metals—nitrates, chlorides, sulphides, sulphates, phosphates, carbonates, etc.—are nearly all soluble in water, although lithium, carbonate, phosphate, and fluoride are very

much less soluble than the corresponding salts of the other members. And in this respect, lithium resembles the members of the calcium family, and it thus forms a connecting or bridge element between the alkalies and alkaline earths. The alkali sulphates form isomorphous characteristic alums (*q.v.*), but lithium alum appears to be so soluble that it has not yet been crystallized. The modes of crystallization of sodium and potassium sulphates and carbonates are worth noting. Lithium carbonate is sparingly soluble in water, sodium carbonate is not deliquescent, the others are. The salts of sodium and lithium form stable hydrates with water, whereas potassium, rubidium, and cæsium salts are nearly all anhydrous. Sodium resembles lithium in the solubility of its chloroplatinate, acid tartrate, and alum so much so that the alkali metals are sometimes divided into two classes : (1) those with sparingly soluble chloroplatinates—viz. potassium, rubidium, and cæsium ; and (2) those with soluble chloroplatinates—viz. sodium and lithium.

TABLE LXIV.—PHYSICAL PROPERTIES OF THE ALKALI METALS.

	Lithium.	Sodium.	Potassium.	Rubidium.	Cæsium.
Atomic weight	6·94	23·00	39·10	85·45	132·81
Specific gravity	0·534	0·9723	0·859	1·525	1·903
Atomic volume	13·1	23·7	45·4	55·8	71·0
Melting point	180°	97·6°	65·5°	39°	28·5°
Boiling point	+1400°	877·5°	757°	696°	670°
Specific heat at 0°	0·941	0·2811	0·1728	0·0802	0·0522
Coefficient expansion	—	0·000274	0·000282	0·000338	0·000345
Heat of fusion (cals.)	—	27·21	14·67	6·144	3·766

INDEX

A

Abraumsalze, 428
Acceleration, period of, 150
Air, marine acid, 20
Alkali bicarbonates, 772
—— bromides, 577
—— carbonates, 710
—— —— acid, 772
—— —— impurities, 724
—— caustic, 495
—— chlorides, 521
—— dihydrorthophosphates, 858
—— dimetaphosphates, 867
—— diphosphates, 862
—— fluorides, 512
—— *hexametaphosphates*, 870
—— hydrocarbonates, 773
—— hydrorthophosphates, secondary, 851
—— hydrosulphates, 677
—— iodides, 596
—— metals, binary alloys, 478
—— —— history, 419
—— —— occurrence, 423
—— —— preparation, 445
—— —— relations, 879
—— metaphosphate, 867
—— mild, 495
—— mineral, 420
—— monosulphide, 621
—— nitrates, 802
—— ortho-phosphates, 847
—— polysulphides, 629
—— pyrophosphate, 862
—— sulphate, 656
—— tetrametaphosphates, 869
—— trimetaphosphates, 869
—— vegetable, 420
—— works, 735
Alkalies, caustic, 421
—— fixed, 420
—— mild, 421
—— volatile, 420
Alloys, alkali metals, 478
Aluandite, 426
Aluminium, bromate, 353
—— chlorate, 353
—— hypochlorite, 275
—— iodate, 353
—— periodate, 415
—— perchlorate, 401
Alunite, 657
Amblygonite, 426
Ammoniacum, 781
Ammonium, 781
—— barium trimetaphosphate, 877
—— biniodide, 233
Ammonium bisulphate, 703
—— bromate, 338
—— bromide, 590
—— —— ammines, 594
—— bromoiodide, 595, 619
—— carbamate, 793
—— carbonate, acid, 787
—— —— half acid, 786
—— —— preparation, 782
—— —— properties, 784
—— carbonates, 780
—— chlorate, 338
—— chloride, 561
—— —— preparation, 562
—— —— properties, 563
—— —— *purification*, 563
—— —— uses, 574
—— chlorite, 284
—— chlorobromide, 595
—— chloroiodide, 619
—— decametaphosphate, 878
—— dihydropyrophosphate, 876
—— dihydrorthophosphate, 871
—— *di-iodate*, 340
—— dimetaphosphate, 876
—— disulphide, 651
—— enneasulphide, 654
—— fluoride, 519
—— —— ammino-, 520
—— heptasulphide, 653
—— hydrobromide, 594
—— hydrocarbonate, 787
—— —— preparations, 787
—— —— properties, 788
—— hydrofluoride, 520
—— hydronitrate, 842
—— hydrorthophosphate, 871
—— hydrosulphate, 703
—— hydrosulphide, properties, 646
—— hypobromite, 270
—— hypochlorite, 96, 270
—— hypoiodite, 270
—— iodate, 339
—— —— hydrated, 340
—— iodatophosphate, 874
—— iodide, 615
—— —— ammine, 619
—— *lithium hydrorthophosphate*, 876
—— —— pentametaphosphate, 878
—— —— periodate, 409
—— —— sulphate, 705
—— —— trimetaphosphate, 877
—— metaphosphate, 876
—— monosulphide, 648
—— —— *ammine*, 650, 651
—— nitrate, 829
—— —— ammine, 843

Ammonium nitrate, properties, chemical, 840
—— —— —— *physical, 833*
—— nitrato-sulphate, 843
—— octosulphide, 654
—— orthophosphate, normal, 874
—— *pentabromide, 595*
—— pentametaphosphate, 877
—— pentasulphide, 652
—— perchlorate, 396
—— periodates, 408, 409, 410
—— perphosphate, 874
—— phosphates, 871
—— potassium decametaphosphate, 876
—— —— dimetaphosphate, 877
—— —— *orthophosphates, 875*
—— —— pentametaphosphate, 877
—— —— pyrophosphate, 876
—— pyrophosphate, 876
—— *sesquicarbonate, 786, 797*
—— sodium dimetaphosphate, 877
—— —— hydrorthophosphate, 874
—— —— orthophosphates, 875
—— —— pentametaphosphate, 877
—— —— *pyrophosphate, 876*
—— —— sesquiphosphate, 876
—— —— sulphate, 706
—— sulphate, 695
—— —— *acid, 703*
—— —— properties, chemical, 701
—— —— —— physical, 696
—— sulphide, 645
—— tetrametaphosphate, 877
—— *tetrasulphide, 652*
—— tetraenneasulphide, 652
—— tribromide, 594
—— tri-iodate, 340
—— *tri-iodide, 619*
—— trimetaphosphate, 877
—— trisulphide, 651
—— —— gold, 651
Amphibole, 2
Anhydrite, 430
Anhydro-iodic acid, 307, 324
Antimony perchlorate, 401
Aphthitalite, 430, *657*
Aqua bromata, 71
—— chlorata, 71
—— chrysulca, 21
—— prima, 20
—— regia, 20
—— salis armoniaci, 20
—— —— nitri, 20
—— secunda, 20
Arcanum duplicatum, 656
Arsenic pentafluoride, 12
Ascharite, 430
Astracanite, 430
—— potassium, 430
Atacamite, 15
Atrun, 710

B

Barilla, 713, 733
Barium-ammonium trimetaphosphate, 877
—— bromate, *346*
—— —— hydrated, 346
—— carbamate, 796
Barium chlorate, 344, 345
—— —— hydrated, 345
—— *chlorite, 284*
—— chlorocarbamate, 796
—— hypobromite, 273
—— hypochlorite, 272
—— *iodate, 347*
—— —— hydrated, 348
—— perchlorate, 399
—— periodates, 412, 413
Beryllium bromate, 350
—— chlorate, 349
—— iodate, 350
—— perchlorate, 400
—— periodate, 414
Bischofite, 15, 430
Bismuthyl perchlorate, 401
Bittern, 525
Black ash, 731
Blanquette, 713
Blasting powder, 826
Bleach-liquor, 244
Bleaching, 243, 262
—— Berthollet's method, 243
—— powder, 244, 258
—— —— constitution, 260
—— —— manufacture, 259
—— —— properties, 260
Blind roaster, 730
Bloedite, 430
Blue salt, 530
Bœumlerite, 431
Boiling points, *solutions with two*, 327
Boleïte, 15
Bones, fluorine in, 2
Boracite, 15, 430
Bromargyrite, 16
Bromates, 296
—— detection, 319
—— preparation, 300
—— properties, 305
—— *uses*, 319
Bromite, 16
Bromic acid, 296
—— —— constitution, 320
—— —— preparation, 296, *300*
—— —— properties, 305
Bromides, acid, 220
—— complex, 228
—— detection, 209
—— preparation, 214
—— properties, 217
—— thermochemistry, 218
Bromine, atomic weight, 101, 105
—— chemical reactions, 90
—— -chlorine compounds, 114
—— *-fluorine compounds, 113*
—— history, 20, 24
—— hydrate, 72
—— *-iodine compounds*, 122
—— mol. wt., 107
—— monoxide, 242
—— occurrence, 15
—— pentoxide, 293
—— physical properties, 46
—— preparation, 38
—— purification, 40
—— *solubility, 72*
—— —— acid soln., 82
—— —— organic solvents, 84

Bromine, solubility, salt soln., 82
—— —— water, 71
—— trifluoride, 113
—— trioxide, 281, 285
—— uses, 96
—— valency, 108
—— water, 71
Bromo-carnallite, 16
Bromoiodides, 237
Bromous acid, 285
—— anhydride, 285
Bromum solidificatum, 97
Bromyrite, 16
Brown powder, 828
Bucking, 243

C

Cadmium bromate, 350
—— —— ammino-, 350
—— chlorate, 350
—— —— ammino-, 350
—— *iodate*, 351
—— —— ammino-, 351
—— *perchlorate*, 400
—— periodate, 414
Cæsium anhydro-iodate, 338
—— at. wt., 470
—— bromide, 577
—— —— properties, chemical, 586
—— —— —— physical, 577
—— bromoiodide, 610
—— carbonate, 725
—— —— properties, chemical, 767
—— —— —— physical, 747
—— chlorate, 326
—— chloride, mol. wt., 555
—— —— preparation, 528
—— —— properties, chemical, 552
—— —— —— physical, 529
—— chlorobromides, 588
—— chloroiodide, 610, 611
—— dihydrorthophosphate, 858
—— dioxide, 487
—— diphosphate, 862
—— disulphide, 631, 632
—— fluoride, 512
—— fluoroperiodates, 417
—— fluorophosphate, 851
—— hexasulphide, 631, 640
—— history, 422
—— hydrocarbonate, 774
—— *hydronitrate*, 821
—— hydrorthophosphate, 851
—— hydrosulphide, 642
—— hydroxide, 495
—— —— properties, 500
—— *iodate*, 333
—— iodato-periodate, 408
—— *iodide*, 596
—— —— properties, chemical, 598
—— —— —— *physical*, 605
—— lithium alloys, 481
—— metaphosphate, 867
—— monosulphide, 622
—— —— hydrated, 624
—— —— properties, chemical, 627
—— —— —— physical, 624
—— monoxide, 486
—— nitrate, 802
Cæsium nitrate properties, chemical, 820
—— —— —— physical, 808
—— orthophosphate, normal, 847
—— —— properties, chemical, 849
—— —— —— physical, 848
—— pentabromide, 588
—— pentaiodide, 610
—— pentasulphide, 631, 638
—— perchlorate, 395
—— periodates, 408
—— -potassium alloys, 481
—— preparation, 449
—— properties, chemical, 468
—— —— physical, 451
—— *pyrophosphate*, 862
—— salts extraction, 442, 444
—— subchloride, 530
—— suboxide, 486
—— sulphate, preparation, 660
—— —— properties, chemical, 672
—— —— —— physical, 660
—— sulphoniodide, 607
—— *tetrasulphide*, 631, 634
—— tetroxide, 485, 491
—— *tribromide*, 587
—— tri-iodide, 609
—— *trioxide*, 485, 491
—— trisulphide, 631, 634
Calcium bromate, 346
—— —— hydrated, 346
—— carbamate, 796
—— chlorate, 344, 345
—— —— hydrated, 345
—— chlorite, 284
—— hydroxyhypochlorites, 272
—— hypobromite, 273
—— hypochlorite, 272
—— hypoiodite, 273
—— iodate, 347
—— —— hydrated, 347
—— perchlorate, 399
—— periodates, 412, 413
Caliche, 17, 803
Calicheras, 803
Calomel, 15
Carbamic acid, 792
Carnallite, 15, 430
Catalysis, 143
—— by hydrochloric acid, 196
Caustic alkali, 495
—— alkalies, 421
Caustification, 497
—— *ionic theory*, 498
—— molecular theory, 498
Cell, Griesheim's, 35
—— Solvay's, 36
—— Sueur's, 35
Cellarius' receiver, 163
Cerargyrite, 15
Ceric iodate, 354
—— perchlorate, 402
Cerium bromate, 355
Cerous bromate, 357
—— *iodate*, 354, 357
—— perchlorate, 402
—— *periodate*, 416
Chatelier's law, 147
Chemical action, kinetic theory, 141, 142
Chhilua, 808
Chiolite, 1

Chlorates, 296
—— detection, 319
—— preparation, 297
—— —— electrolytic process, 298
—— properties, 305
—— uses, 319
Chloric acid, 296
—— —— constitution, 320
—— —— preparation, 296, 299
—— —— properties, 305
Chlorides, acid, 219
—— complex, 228
—— detection, 209
—— preparation, 214
—— properties, 217
—— thermochemistry, 218
Chlorine, Acker's process, 36
—— active, 156
—— and hydrogen, union in light, 148
—— atomic weight, 101
—— -bromine compounds, 114
—— Castner's process, 36
—— chemical reactions, 90
—— Deacon's process, 31
—— dioxide, 286
—— —— composition, 290
—— —— preparation, 287
—— —— properties, 288
—— electrolytic processes, 34
—— -fluorine compounds, 113
—— history, 20
—— hydrate, 72
—— -iodine compounds, 114
—— *isotopes, 105*
—— liquefaction, 51
—— *Mond's process*, 34
—— mol. wt., 107
—— monoxide, 240
—— —— composition, 242
—— —— properties, 241
—— occurrence, 15
—— pentoxide, 293
—— peroxide, 286
—— physical properties, 46
—— preparation, 25
—— purification, 26
—— solubility, 72
—— —— acid soln., 82
—— —— organic solvents, 84
—— —— salt soln., 82
—— —— water, 71
—— tetroxide, 287
—— trioxide, 281
—— uses, 96
—— valency, 108
—— water, 71
—— Weldon and Péchiney's process, 34
—— Weldon's process, 28
Chlorinated potash, 243
—— soda, 244
Chlorites, 283
Chloroapatite, 15
Chlorobromides, 237
Chlorocalcite, 15
Chlorochroite, 657
Chlorogen, 268
Chloroiodides, 237
Chlorophane, 3
Chloros, 96
Chlorous acid, 281
Chlorous anhydride, 281
Chlorozone, 268
Chromato-iodic acid, 363
Chromic perchlorate, 403
Chromium bromate, 358
—— chlorate, 357
—— iodate, 358
Cineres clavellati, 419
Coba, 803
Cobalt, bromate, 360
—— —— ammino-, 360
—— chlorate, 360
—— —— ammino-, 360
—— iodate, 361
—— —— ammino-, 362
—— perchlorate, 404
—— —— *ammino-*, 404
Coccinite, 17
Cocoa powder, 828
Colloidal iodine, 98
Colour changes on heating, 221
Compounds, molecular, 223
Confitello, 711
Conjelo, 803
Contact action, 143
Cookeite, 426
Copper bromate, 343
—— —— ammino-, 343
—— hypobromite, 271
—— iodate, 343
—— —— ammino-, 344
—— —— hydrated, 343
—— oxyiodate, 344
—— *periodates*, 412
Coprolites, 1
Costra, 803
Cotunnite, 15
Crofting, 243
Cryolite, 1
—— ash, 715
Cryophylite, 426
Crystallization, magnesium and potassium chlorides, 432
—— —— —— —— sulphates, 432
—— of mixed salts, 431
—— —— solutions of magnesium and potassium chlorides and sulphates, 434
—— ponds, 525
Crystalloluminescence, 531
Crystals, mixed, 224
Cumengeïte, 15
Cupric chlorate, 342
—— —— ammino-, 343
—— —— hydrated, 342
—— hypochlorite, 271
—— oxychlorate, 342
—— perchlorate, 399
—— —— ammino-, 399
Cyanochroite, 657
Cyanochrome, 657

D

Darapskite, 656, 804, 816
Daubreïte, 15
Dead space in reactions, 312
Dephlogisticated muriatic acid, 21
Dhobies earth, 710
Di-iodates, 324

Didymium bromate, 354
—— *perchlorate*, 402
Dietzeite, 347
Digestive salt of Sylvius, 420
Dimesoiodic acid, 324
Dissociation, 143
Diver's liquid, 843
Douglasite, 15, 430
Duka, 711
Dy*namite*, 829
Dysprosium bromate, 354

E

Eau de Javelle, 243, 268
—— —— Labarraque, 244, 268
Eglestonite, 15
Electro-affinity, 227
Electrozone, 96
Embolite, 16
English drops, 781
Epsomite, 430
Equilibria, chemical, effect of press., 146
—— —— —— —— temp., 145
Equilibrium, 141
—— condition of, 141
—— false, 162
—— law, *J. H. van't Hoff's*, 145
Erbium bromate, 354
—— chlorate, 354
—— *iodate*, 354
Eryophylite, 426
Erythrosiderite, 15
Espumilla, 711
Eucryptite, 425

F

Ferment, nitric, 807
—— *nitrous*, 807
Ferric bromate, 359
—— *chlorate*, 359
—— hypochlorite, 275
—— iodate, 359
—— perchlorate, 403
—— periodate, 416
Ferronatrite, 656
Ferrous bromate, 359
—— chlorate, 359
—— iodate, 359
—— perchlorate, 403
—— periodate, 416
Fiedlerite, 15
Fixed alkalies, 420
Fluellite, 1
Fluor, 1
—— *acid*, 3
—— apatite, 1
—— lapis, 3
Fluorides, 137
—— acid, 138
—— complex, 138
—— detection, 135
—— determination, 135
—— double, 138
—— etching test, 135
—— hydroxy-, *139*
—— oxy-, 139
—— thermochemistry, 218
Fluorides, uses, 134
Fluorine, 3, 4
—— action, acetone, 13
—— —— ammonia, 12
—— —— arsenic, 12
—— —— —— trichloride, 12
—— —— —— *trifluoride*, 12
—— —— —— trioxide, 12
—— —— borates, 13
—— —— *boric oxide*, 12
—— —— *boron*, *12*
—— —— —— trichloride, 12
—— —— bromides, 13
—— —— bromine, 12
—— —— calcium carbide, 3
—— —— carbon, 12, 13
—— —— —— dioxide, 13
—— —— —— disulphide, 13
—— —— —— monoxide, 13
—— —— —— tetrachloride, 13
—— —— *carbonates*, 13
—— —— carbonyl chloride, 13
—— —— chlorides, 13
—— —— chlorine, 11
—— —— chloroform, 13
—— —— cyanides, 13
—— —— cyanogen, 13
—— —— ethylene tetrachloride, 13
—— —— *glass*, 12
—— —— hydrofluoric acid, 12
—— —— hydrogen, 11
—— —— —— *bromide*, 12
—— —— —— chloride, 12
—— —— —— *iodide*, 12
—— —— —— sulphide, 11
—— —— iodides, 13
—— —— iodine, 12
—— —— metals, 13
—— —— nitrates, 13
—— —— *nitrides*, 13
—— —— nitrogen, 12
—— —— —— peroxide, 12
—— —— *nitrous oxide*, 12
—— —— oxides, 13
—— —— oxygen, 11
—— —— ozone, 11
—— —— phosphates, 13
—— —— phosphides, 13
—— —— phosphorus, 12
—— —— —— oxyfluoride, 12
—— —— —— *pentachloride*, 12
—— —— —— pentafluoride, 12
—— —— —— pentoxide, 12
—— —— —— *trichloride*, 12
—— —— selenium, 11
—— —— silica, 12
—— —— silicon, 12
—— —— —— tetrachloride, 12
—— —— sulphates, 13
—— —— sulphides, 13
—— —— sulphur, *11*
—— —— —— dioxide, 11
—— —— sulphuric acid, 11
—— —— tellurium, 11
—— —— water, 11
—— atomic weight, 13
—— boiling point, 10
—— -bromine compounds, 113
—— capillarity, 10
—— -chlorine compounds, 113

Fluorine, colour, 9
—— decomposition voltage, 10
—— density (relative), 10
—— dispersion, 10
—— elementary nature, 9
—— expansion (thermal), 10
—— history, 3
—— in bones, 2
—— —— mineral waters, 2
—— index of refraction, 10
—— iodine compounds, 114
—— magnetic susceptibility, 10
—— melting point, 10
—— molecular weight, 13
—— occurrence, 1
—— preparation, 7
—— —— Arago's process, 9
—— —— Moissan's process, 8
—— —— Poulenc and Meslans' process, 9
—— properties, chemical, 10
—— —— physical, 9
—— refraction, 10
—— smell, 9
—— *spectrum*, 10
—— transport number, 10
Fluorite, 1, 3
Fluorium, 4
Fluoro-iodic acid, 363
Fluorspar, 1, 3
Fluss, 3
Flusspat, 3
Flusssäure, 3
Flussspath, hepatic, 1
—— stink, 1
Footeïte, 15
Fuming acids, 190

G

Glaserite, 430, 657, 688
Glasspat, 3
Glauberite, 430
Gold hypochlorite, 271
—— iodate, 342
Gun-cotton, 829
Gunpowder, 820, 825
Gypsum, 430

H

Halazone, 97
Halide salts, 1
Halides, 1
Halite, 15, 430, 522
Halogens, 1
—— binary compounds, 113
Haloid salts, 1
Hanksite, 656
Hardness, 453
Heinzite, 430
Herderite, 2
Hermite's fluid, 96
Heterosite, 426
Hiddenite, 425
Hieratite, 2
Hollands, 243
Horn silver, 15
Hurka, 711
Hydriodic acid, preparation, 170
—— —— properties, 182
Hydriodic acid, uses, 212
Hydroboracite, 430
Hydrobromic acid, preparation, 167
—— —— properties, 182
—— —— uses, 212
Hydrochloric acid, impurities in, 165
—— —— preparation, 158
—— —— properties, 182
—— —— purification, 165
—— —— uses, 212
Hydrofluoric acid, 127
—— —— chemical properties, 133
—— —— physical properties, 129, 130
—— —— preparation, 127
—— —— uses, 134
Hydrogen and chlorine, union in light, 148
—— bromide, hydrates, 184
—— —— non-aq. soln., 197
—— —— physical properties, 173
—— —— preparation, 167
—— —— properties, chemical, 200
—— —— solubility, 182
—— chloride, composition, 208
—— —— hydrates, 182
—— —— non aq. soln., 196
—— —— physical properties, 173
—— —— *preparation*, 158
—— —— properties, chemical, 200
—— —— solubility, 182
—— *chlorobromide*, 234
—— fluoride, 127
—— —— chemical properties, 133
—— —— composition, 134
—— —— mol. wt., 134
—— —— physical properties, 129
—— —— preparation, 127
—— iodide, hydrates, 185
—— —— non-aq. soln., 197
—— —— physical properties, 173
—— —— preparation, 170
—— —— properties, chemical, 200
—— —— purification, 172
—— —— solubility, 182
—— perbromide, 234
—— perchloride, 234
—— periodide, 234
Hydromelanthallite, 15
Hydroxylamine chlorite, 284
Hyperoxygenized muriatic acid, 286
Hypobromites, 250, 267
—— preparation, electrical processes, 280
—— uses, 256
Hypobromous acid, preparation, 243, 245
—— —— properties, 250
—— anhydride, 242
Hypochlorites, 250, 267
—— constitution, 257
—— preparation, electrical processes, 276
—— uses, 256
Hypochlorous acid, preparation, 243, 244
—— —— properties, 250
—— anhydride, 241
Hypoiodique anhydride, 291
Hypoiodites, 250, 267
—— preparation, electrical processes, 280
Hypoiodous acid, preparation, 243, 246
—— —— properties, 250
—— anhydride, 242
Hypotribromites, 252
Hypotri-iodites, 252

Indium iodate, 355
—— perchlorate, 402
Induction period, 149
—— —— of photochemical, 149
Iodammonium iodide, 620
—— —— *ammine, 620*
Iodates, 296
—— acid, 324, 335
—— complex, 324
—— detection, 319
—— preparation, 301
—— properties, 305
—— uses, 319
Iodic acid, 296
—— —— chromato-, 363
—— —— constitution, 320
—— —— fluoro-, 363
—— —— molybdate-, 363
—— —— phosphate-, 363
—— —— preparation, 296, 301
—— —— properties, 305
—— —— selenato-, 363
—— —— sulphate-, 363
—— —— tellurato-, 363
—— —— tungstate-, 363
—— —— vanadato-, 363
Iodides, acid, 220
—— complex, *229*
—— detection, 209
—— preparation, 214
—— properties, 217
—— thermochemistry, 218
Iodine acetate, 292
—— α-monochloride, 116
—— *β-monochloride, 116*
—— atomic weight, 101, 106
—— -bromine compounds, 122
—— chemical reactions, 90
—— -chlorine compounds, 114
—— colloidal, 98
—— dioxide, 291
—— —— preparation, 291
—— —— properties, 292
—— *extraction from caliche,* 43
—— —— —— seaweed, 42
—— -fluorine compounds, 114
—— history, 20, 23
—— hydrosol, 98
—— iodate, 285, 292
—— isotopes, *107*
—— mol. wt., 107
—— monobromide, *122*
—— —— preparation, 116
—— —— properties, 117
—— monoxide, 242
—— nitrate, 292
—— *occurrence,* 16
—— oxyfluoride, 292
—— pentafluoride, 114
—— pentoxide, 293
—— —— *preparation,* 293
—— —— properties, 294
—— physical properties, 46
—— preparation, 41
—— purification, 44
—— *recovery,* 44
—— solubility, 72
—— —— acid soln., 82
Iodine solubility, organic solvents, 84
—— —— salt soln., 82
—— —— water, 71
—— solutions, colour, 110
—— sulphate, 285
—— —— Millon's, 292
—— sulphite, 292
—— *tetroxide, 291*
—— trichloride, 119
—— trioxide, 281, 285
—— uses, 96
—— valency, *108*
Iodobromite, 16, 17
Iodoembolite, 16
Iodonium, 108
—— hydroxide, *108*
—— phenyl derivatives, 108
Iodosobenzene, 108
Iodous acid, 285
Iodyrite, *17*
Ions, nature, 226
Irvingite, 425

K

Kainite, 430, 657
Kali carbonicum e tartaro, 714
—— *magnesia,* 660
Kalinite, 657
Kalk flussäurer, 3
Kara, 711
Karstenite, 430
Kelp ash, 437
Kieserite, 430
Kodolite, 2
Koenenite, 431
Kremersite, 15
Krugite, 430, 657
Kunzite, 425

L

Langbeinite, *430*
Lanthanum *bromate,* 354
—— iodate, 355
—— perchlorate, 402
—— periodate, 415
Laurionite, 15
Lautarite, 347
Lawrencite, 15
Lead bromate, 356
—— *chlorate,* 356
—— chlorite, 283
—— iodate, 356
—— perchlorate, 402
—— *periodate, 415,* 416
Least effort, *principle* of, 146
Leonite, 430, 657
Lepidolite, 2, 425
Lithiophylite, 426
Lithium, *α*-, 458
—— ammonium hydrorthophosphate, 876
—— —— pentametaphosphate, 878
—— —— sulphate, 705
—— —— trimetaphosphate, 877
—— at. wt., 470
—— *β*-, 458
—— bromate, 330

Lithium bromide, 577
—— —— ammines, 586
—— —— properties, chemical, 586
—— —— —— physical, 579
—— -cæsium alloys, 481
—— carbamate, 796
—— carbonate, preparation, 725
—— —— properties, chemical, 767
—— —— —— physical, 747
—— chlorate, 325
—— —— ammino, 329
—— chloride ammino-, 554
—— —— and sulphate crystallization, 689
—— —— hydrated, 542
—— —— preparation, 528
—— —— properties, chemical, 552
—— —— —— physical, 529
—— chlorite, 284
—— chloroiodide, 611
—— dihydrorthophosphate, 858
—— dioxide, 487
—— diphosphate, 862
—— disulphide, 632
—— fluoride, 512
—— history, 421
—— hydrides, 481
—— hydrocarbonate, 773
—— hydrorthophosphate, secondary, 851
—— hydrosulphates, 678, 679
—— —— hydrated, 687
—— hydrosulphide, 641
—— hydroxide, 495
—— —— properties, 500
—— hydroxyiodide, 600
—— hypochlorites, 269
—— iodate, 332
—— —— hydrated, 334
—— iodatophosphate, 851
—— iodide, 596
—— —— hydrated, 602
—— —— properties, chemical, 605
—— —— —— physical, 598
—— metaphosphate, 867
—— monosulphide, 621
—— —— properties, chemical, 627
—— —— —— physical, 624
—— monoxide, 486
—— nitrate, 802
—— —— hydrates, 815
—— —— properties, chemical, 820
—— —— —— physical, 808
—— nitratosulphate, 816
—— orthophosphate, normal, 847
—— —— —— properties, chemical, 849
—— —— —— —— physical, 848
—— perchlorate, 395
—— periodate, 406, 408, 409
—— —— ammonium, 409
—— -potassium alloys, 480
—— —— carbonate, 748, 768
—— —— sulphate, 687
—— preparation, 445, 449
—— properties, chemical, 468
—— —— physical, 451
—— pyrophosphate, 862
—— -rubidium alloys, 481
—— —— sulphate, 688
—— salts, extraction, 442, 443, 444
—— -sodium alloys, 480
—— —— sulphate, 687
Lithium subchloride, 530
—— sulphate, hydrates, 667
—— —— preparation, 660
—— —— properties, chemical, 672
—— —— —— physical, 660
—— sulphoniodide, 607
—— tetrametaphosphate, 867
Lithophosphorus, 3
Liver of sulphur, 621
—— soda, 621
—— volatile, 645
Lörvite, 430

M

Magnesium and potassium chlorides, crystallization, 432
—— —— —— —— and sulphates, crystallization, 434
—— —— —— sulphates, crystallization, 432
—— bromate, 350
—— chlorate, 349
—— hypobromite, 274
—— hypochlorite, 273
—— hypoiodite, 274
—— iodate, 350
—— perchlorate, 400
—— periodate, 414
Manganato periodic acid, 416
Manganese bromate, 359
—— chlorate, 359
—— —— ammino-, 359
—— dioxide. Action hydrochloric acid, 27
—— iodate, 359
Mangani-iodic acid, 359
Manganic periodate, 416
Manganous perchlorate, 403
Marshite, 17
Matlockite, 15
Melanothallite, 15
Melinophane, 2
Mendipite, 15
Mendozite, 656
Mercuric bromate, 352
—— chlorate, 351
—— chlorite, 284
Mercurius animalis, 780
Mercury hypochlorite, 274
—— hypoiodite, 274
—— iodate, 352
—— perchlorate, 400
—— periodate, 415
Mercurous bromate, 352
—— chlorite, 284
—— iodate, 352
—— periodate, 415
Mesoiodic acid, 322
Mesoperiodic acid, 386
Metachromatism, 221
Metaiodic acid, 322, 324
Metaperiodic acid, 386
Metal of salt, 421
Mild alkali, 495
—— alkalies, 421
Millon's iodine sulphate, 292
Mimetite, 15
Mineral alkali, 420
Mirabilite, 656

Molybdato-iodic acid, 363
—— -periodates, 406, 417
Molysite, 15
Muriatic acid, 20, 21

N

Nantokite, 15
Natar, 419
Natroamblygonite, 426
Natron, 710
Natrophylite, 426
Neodymium bromate, 354
—— perchlorate, 402
Neter, 419
Nickel bromate, 360
—— —— ammino-, 361
—— chlorate, 360
—— —— ammino-, 360
—— iodate, 362
—— —— ammino-, 363
—— —— α-dihydrated, 362
—— —— β-dihydrated, 362
—— perchlorate, 403
—— —— ammino-, 404
—— periodate, 416
Nitratin, 802
Nitre, 419
—— basin, 803
—— beds, 808
—— -cake, 657
—— cubic, 808
—— meal, 807
—— plantations, 808
—— prismatic, 808
—— rhombohedral, 808
Nitric ferment, 807
Nitrocellulose, 829
Nitroglauberite, 691, 803, 816
Nitroglycerol, 829
Nitron, 419
Nitroso-iodic acid, 291
Nitrosyl *perchlorate*, 401
Nitrotoluene, 829
Nitrous ferment, 807
Nitrum, 419
—— flammans, 829
—— vitriolatum, 656
Nocerine, 2

O

Offa Helmonti, 800
Oleum vini, 21
Optical extinction, 155
Orthoiodic acid, 322
Orthoperiodic acid, 386
Ostwald's law of successive reactions, 371
Oxiodic acid, 293
Oxolith, 253
Oxy-acids of chlorine, *substitution of* **bromine, 385**
—— —— —— —— —— **iodine, 385**
Oxychlorine acids, thermochemistry, 379
Oxygenated potassium chlorate, 371
Oxyiodine, 293

P

Pachnolite, 1
Panacea duplicata, 656
Pan acid, 730
—— gas, 730
Paralaurionite, 15
Paraperiodic acid, 386
Partition coeff., 75
—— law, 75
—— —— Berthelot and Jungfleisch, 75
Pearlash, 438
Penfieldite, 15
Perbromates, 384
Perbromic acid, 384
Perbromides, 233
Perchlorates, 370, 395
—— detection, 381
—— determination, 381
—— preparation, 371
—— —— electrolytic processes, 3
—— *properties*, 381
Perchloric acid, 370
—— —— *composition*, 382
—— —— constitution, 382
—— —— hydrates, 378
—— —— preparation, 371
—— —— *properties, chemical*, 379
—— —— —— physical, 376
—— anhydride, 380
Perchlorides, 233
Percylite, 15
Period of acceleration, 150
—— —— induction, 311
—— —— —— photochemical, 149
Periodates, 386, 406
—— , *Molybdato-*, 417
—— nomenclature, 386
—— preparation, 387
—— Tungstato-, 417
Periodic acid, detection, 393
—— —— determination, 393
—— —— meso-, 386
—— —— meta-, 386
—— —— nomenclature, 386
—— —— ortho-, 386
—— —— para-, 386
—— acids, 386
—— —— basicity of, 391
—— —— *preparation*, 387
—— —— properties, 389
Periodides, 233
Perlatum, 851
Petalite, 425
Phosgenite, 15
Phosphato-iodic acid, 363
Phosphoric spar, 3
Phosphorite, 1
Photochemical equivalence, 153
—— —— **Einstein's law, 153**
—— **extinction, 155**
—— **induction, 149**
Photoelectric action, 152
—— —— **effect, 152**
***Photolysis*, 154**
***Picromerite*, 430, 657**
***Pinnoite*, 430**
Plate sulphate, 688
Pneumatogen, 480
Pollucite, 426

Pollux, 426
Polyhalite, 430, 657
Polyiodides, 233
Potash, 420, 438
—— salt beds, 427
Potassium ammonium decametaphosphate, 878
—— —— *orthophosphates*, 875
—— —— pentametaphosphate, 877
—— —— pyrophosphate, 876
—— and magnesium chlorides, crystallization, 432
—— —— —— —— and sulphates, crystallization, 434
—— —— —— sulphates, crystallization, 432
—— —— sodium sulphates and chlorides, crystallization, 689
—— *-astracanite*, 430
—— at. wt., 470
—— bromate, 330
—— bromide, 577
—— —— impurities of, 578
—— —— properties, chemical, 586
—— —— —— physical, 579
—— bromoiodide, 610
—— -cæsium alloys, 481
—— carbamate, 796
—— carbonate and sodium nitrate reaction, 804
—— —— hydrated, 756
—— —— preparation, 713
—— —— properties, chemical, 767
—— —— —— physical, 747
—— carbonyl, 450
—— chlorate, 326
—— chlorates, 297
—— chloride and sodium sulphate crystallization, 689
—— —— extraction from carnallite, 526
—— —— mol. wt., 555
—— —— occurrence, 522
—— —— preparation, 528
—— —— properties, 529
—— —— —— chemical, 552
—— —— —— physical, 529
—— —— purification, 527
—— chlorite, 283
—— chloroiodide, 610, 611
—— chlorosulphate, 691
—— dihydrorthophosphate, 858
—— dihydropyrophosphate, 865
—— di-iodate, 335
—— dioxide, 487
—— diphosphate, 862
—— disulphide, 630, 632
—— fluoride, 512
—— fluorometaphosphate, 867
—— fluorophosphate, 850
—— fluorosulphate, 691
—— hexasulphide, 630, 640
—— history, 421
—— hydride, 481
—— hydrobromide, 587
—— hydrocarbonate, 763, 774, 778
—— hydronitrate, 821
—— *hydrorthophosphate, secondary*, 851
—— hydrosulphate, hydrated, 682
—— hydrosulphates, 677, 678, 679, 682
—— hydrosulphide, 641
Potassium hydroxide, 495
—— —— properties, 500
—— —— purification, 499
—— —— uses, 509
—— hypobromite, 269
—— hypoiodite, 269
—— iodate, 332
—— —— hydrated, 335
—— iodatophosphate, 851
—— iodatosulphate, 691
—— iodide, 596
—— —— impurities, 598
—— —— properties, chemical, 605
—— —— —— physical, 598
—— iodosulphate, 691
—— -lithium alloys, 480
—— —— carbonate, 748, 768
—— —— sulphate, 687
—— *manganato-periodate*, 416
—— metaphosphate, 867
—— monosulphide, 622
—— —— hydrated, 624
—— —— *properties*, chemical, 627
—— —— —— physical, 624
—— monoxide, 485
—— nitrate, 802
—— nitrates, properties, chemical, 820
—— —— —— physical, 808
—— occurrence, 423
—— *orthophosphate, normal*, 847
—— —— properties, chemical, 849
—— —— —— physical, 848
—— pentasulphide, 630, 636
—— perchlorate, 395
—— periodates, 407, 409, 410
—— preparation, 445, 447
—— properties, chemical, 468
—— —— physical, 451
—— pyrophosphate, 862
—— rubidium alloys, 481
—— salts, extraction, 437
—— —— —— blast furnace dust, 440
—— —— —— brines, 437
—— —— —— cement kiln dust, 440
—— —— —— insoluble silicates, 439
—— —— —— kelp ash, 437
—— —— —— sea water, 437
—— —— —— suint, 438
—— —— —— vinasse of sugar beet, 438
—— —— —— wood ashes, 437
—— —— —— wool fat, 438
—— sesquicarbonate, 778
—— sodide, 480
—— -sodium alloys, 480
—— —— carbonate, 769
—— —— chlorosulphate, 691
—— —— dimetaphosphate, 877
—— —— hydrorthophosphate, 857
—— —— pyrophosphate, 867
—— —— sesquiphosphate, 850
—— —— sulphate, 688
—— subchloride, 530
—— suboxide, 485
—— sulphate and sodium chloride, crystallization, 689
—— —— occurrence, 657
—— —— preparation, 659
—— —— properties, chemical, 672
—— —— —— physical, 660
—— sulphoniodide, 607

Potassium *tetrametaphosphate*, 867
—— tetrasulphide, 630, 634
—— *tetroxide*, 485, 491
—— tribromide, 587
—— tri-iodate, 336
—— *tri-iodide*, 609
—— trioxide, 485, 491
—— trisulphide, 630, 633
—— *uranyl iodate*, 358
—— uses, 470
Praseodymium bromate, 354
—— perchlorate, 402
Pressure, effect on equilibria, 146
Principle of least effort, 146
Prism powder, 826
Prosopite, 1
Pseudobolite, 15
Pseudotriplite, 426
Purification of gases by fractional solidification, 172
Pyroemerald, 3
Pyroiodic acid, 324
Pyromorphite, 15
Pyrosmalite, 15

R

Rafaelite, 15
Ralstonite, 1
Reaction, bimolecular, 141
—— Landolt's, 311
—— *unimolecular*, 49
Reactions, coupled, 240
—— dead space in, 312
—— law of successive, 371
—— light, primary, 153
—— —— secondary, 152
Rhodizite, 426
Richardite, 430
Rinneite, 15
Roaster acid, 730
Robin's law, 146
Rock salt, 430, 522
—— —— winning, 525
Rubellite, 426
Rubenglimmer, 426
Rubidium, at. wt., 470
—— bromide, 577
—— —— properties, chemical, 586
—— —— —— physical, 577
—— bromoiodide, 610
—— -cæsium alloys, 481
—— carbonate, 725
—— —— properties, chemical, 767
—— —— —— physical, 747
—— *chlorate*, 326
—— chloride, mol. wt., 555
—— —— preparation, 528
—— —— properties, chemical, 552
—— —— —— physical, 529
—— chlorobromides, 588
—— *chloroiodide*, 610, 611
—— di-iodate, 337
—— dioxide, 487
—— *dihydrorthophosphate*, 858
—— diphosphate, 862
—— disulphide, 631, 632
—— *duoride*, 512
—— fluorophosphate, 851
Rubidium hexasulphide, 631, 640
—— history, 422
—— hydrocarbonate, 774
—— hydronitrate, 821
—— hydrorthophosphate, 851
—— *hydrosulphide*, 642
—— hydroxide, 495
—— —— properties, 500
—— *iodate*, 333
—— iodide, 596
—— —— properties, chemical, 605
—— —— —— physical, 598
—— -lithium alloys, 481
—— —— sulphate, 688
—— metaphosphate, 867
—— monosulphide, 622
—— —— hydrated, 624
—— —— properties, chemical, 627
—— —— —— physical, 624
—— monoxide, 486
—— nitrate, 802
—— —— properties, chemical, 820
—— —— —— physical, 808
—— orthophosphate, normal, 847
—— —— —— *properties, chemical*, 849
—— —— —— —— physical, 848
—— pentasulphide, 631, 638
—— perchlorate, 395
—— periodates, 407
—— potassium alloys, 481
—— *preparation*, 448
—— properties, chemical, 468
—— —— physical, 451
—— pyrophosphate, 862
—— salts, extraction, 442, 444
—— subchloride, 530
—— sulphate, preparation, 660
—— —— properties, chemical, 672
—— —— —— physical, 660
—— sulphoniodide, 607
—— *tetrasulphide*, 631, 634
—— tetroxide, 485, 491
—— tribromide, 587
—— tri-iodate, 338
—— tri-iodide, 609
—— trisulphide, 631, 634

S

Sajji-mati, 710
Sal ammoniac, 15
—— *armeniacus*, 20
—— de duobus, 656
—— excoctus, 522
—— fossilis, 522
—— —— *pellucens*, 522
—— gemma, 522
—— lacustus, 522
—— marinus, 522
—— microcosmicum, 874
—— mirabile Glauberi, 656
—— muriaticum, 522
—— petræ, 420
—— *polychrestum Glaseri*, 656
—— prunella, 656
—— tartari, 656, 714
—— urinæ fixum, 874
—— volatile, 780
—— —— cornu cervi, 781

Salicor, 713
Salis natura, 20
Salt, 521
—— cake, 657, 730, 731
—— *cerebros-*, *526*
—— decrepitating, 533
—— fish-, 526
—— gardens, 525
—— Glauber's, 656
——-lock, 522
—— meadows, 525
—— *Metal of*, *421*
—— of Sylvius, 420
—— —— tartar, 656, 714
—— pickling, 807
—— ponds, 525
—— prunella, 656
—— springs, 522
—— Sylvius' digestive, 522
—— table-, 526
Saltpetre, 420
—— Bengal, 808
Salts, complex, 223, 224
—— compound, 223
—— double, 223, 224
—— mixed, 264
Samarium bromate, 354
—— *iodate*, *355*
—— periodate, 415
Scæchite, 15
Scandium bromate, 353
—— chlorate, 353
—— iodate, 353
—— *perchlorate*, *402*
Schönite, 430, 657
Schwartzembergite, 17
Sea salt, 522
—— water, 437
Sebkainite, 429
Sel de varec, 713
—— *febrifuge*, *522*
—— gemme, 522
Selenato-di-iodic acid, 363
—— monoiodic acid, 363
Sellaite, 1
Sels mixtes, 525, 657, 658
Sicklerite, 426
Sidero natrite, 656
Silver bromate, 340
—— —— ammino-, 341
—— chlorate, 340
—— —— ammino-, 340
—— chlorite, 283
—— —— ammino, 284
—— hypobromite, 271
—— hypochlorite, 271
—— *hypoiodite*, *271*
—— iodate, 341
—— perchlorate, 399
—— —— ammino-, 399
—— periodates, 410, 411, 412
Smokeless powders, 829
Soda, 421,
—— alicante, 713
—— cartagena, 713
—— malaga, 713
Sodalite, 15
Sodium α-, 458
—— ammonium dimetaphosphate, 877
—— —— hydrorthophosphate, 874
Sodium ammonium orthophosphates, 875
—— —— pentametaphosphate, 877
—— —— pyrophosphate, 876
—— —— sesquiphosphate, 876
—— —— *sulphate*, *706*
—— and potassium chlorosulphate, 691
—— —— —— sulphates and chlorides, crystallization, 689
—— anhydro-iodate, 337
—— at. wt., 470
—— β-, 458
—— *bromate*, *330*
—— bromide, 577
—— —— properties, chemical, 586
—— —— —— physical, 579
—— carbamate, 796
—— carbonate, α-heptahydrate, 753
—— —— β-heptahydrate, 753
—— —— *ammonia process*, *737*
—— —— hydrates, 751
—— —— in plant ashes, 713
—— —— Leblanc's process, 728
—— —— origin natural, 712
—— —— preparation, 713
—— —— *properties, chemical*, 767
—— —— —— physical, 747
—— —— purification, 724
—— —— Solvay's process, 737
—— carbonato-phosphate, 851
—— chlorate, 325
—— chloride ammino-, 554
—— —— and potassium sulphate, crystallization, 689
—— —— hydrated, *542*, *563*
—— —— mol. wt., 555
—— —— occurrence, 522
—— —— preparation, 528
—— —— properties, chemical, 552
—— —— —— physical, 529
—— —— purification, 527
—— —— separation from brine, *525*
—— —— —— sea-water, 525
—— chlorite, 283
—— chloroiodide, 611
—— dihydropyrophosphate, 865
—— dihydrorthophosphate, 858
—— di-iodate, 337
—— dimetaphosphate, 867
—— dioxide, 487
—— diphosphate, 862
—— *disulphide*, *630*, *632*
—— fluoride, 512
—— fluorophosphate, 850
—— fluorosulphate, 691
—— hexametaphosphate, 870
—— hexasulphide, 630, 640
—— history, 421
—— hydrides, 481
—— hydrocarbonate, 763, 773
—— hydrorthophosphate, 850
—— —— secondary, 851
—— hydrosulphates, 677, 678, 679, 680
—— —— hydrated, 686
—— hydrosulphide, 641
—— hydroxide, 495
—— —— properties, 500
—— —— purification, 499
—— —— uses, 509
—— hypobromite, 269
—— hypochlorite, 269

Sodium iodate, 332
— — hydrated, 334
— iodatophosphate, 851
— iodide, 596
— — hydrated, 602
— — properties, chemical, 605
— — — physical, 598
— -lithium alloys, 480
— — sulphate, 539
— manganato-periodate, 416
— metaphosphate, 867
— monosulphide, 621
— — hydrated, 623
— — properties, chemical, 627
— — — physical, 624
— monoxide, 485
— nitrate, 802
— — and potassium carbonate reaction, 804
— — extraction, 804
— — properties, chemical, 820
— — — physical, 808
— nitratosulphate, 691, 816
— occurrence, 423
— orthophosphate normal, 847
— — — properties, chemical, 849
— — — — physical, 848
— pentaiodide, 610
— pentasulphide, 630, 637
— perchlorate, 395
— periodates, 406, 407, 409, 410
— peroxynitrate, 816
— polyphosphate, 866
— -potassium alloys, 480
— — carbonate, 769
— — hydrorthophosphate, 857
— — pyrophosphate, 866
— — sesquiphosphate, 850
— — sulphate, 687
— preparation, 445, 447
— — electrolytic process, 447
— — — — Castner's, 447
— properties, chemical, 468
— — physical, 451
— pyrophosphate, 862
— sesquicarbonate, 777
— sesquiphosphate, 850
— subchloride, 530
— suboxide, 485
— sulphate, 656
— — α-, 661
— — β-, 661
— — and potassium chloride crystallization, 689
— — hydrates, 667
— — occurrence, 656
— — preparation, 657
— — properties, chemical, 672
— — — physical, 660
— sulphoniodide, 607
— tetrametaphosphates, 867
— tetrasulphide, 630, 634
— trihydropyrophosphate, 865
— tri-iodate, 337
— trimetaphosphate, 869
— trioxide, 485, 491
— trisulphide, 630, 633
— uses, 470
Solid solutions, 224
Solutions, congruent, 740
— incongruent, 740
Sombrerite, 1
Sool, 427
Sosa-bruta, 711
Soude bourde, 713
— d'Argues-mortes, 713
— de Narbonne, 713
— douce, 713
— mélangée, 713
Souring, 243
Soushypoiodique oxyde, 285
Spat *fusible*, 3
Spatum vitreum, 3
Specificum purgans Paracelsi, 656
Spectra, halogens, 57
Spirit of hartshorn, 781
— — salt, rectified, 21
Spiritus animalis, 780
— fumans Berguin's, 645
— — Boyle's, 645
— salis, 20
— — lotii, 780
— — urinæ, 780
— urinæ, 780
— vitrioli coagulabilis, 656
— volatilis salis armoniaci, 780
Spodumene, 425
Sporting powder, 826
Stability constant, 227
Stannic chlorate, 356
Stannous chlorate, 356
Staffelite, 2
Starch, iodide, 99
— iodized, 98
Stassfurt potash beds, 428
— salts, origin, 434
— — uses, 435
Stassfurtite, 430
Steinsalz, 430
Stinkstone, 431
Strontium bromate, 346
— — hydrated, 346
— carbamate, 796
— chlorate, 344
— — hydrated, 345
— chlorite, 284
— hypobromite, 273
— hypochlorite, 272
— iodate, 347
— — hydrated, 348
— perchlorate, 399
— periodates, 412, 413
Strüvenite, 656
Subbromides, 238
Subchlorides, 238
Subiodides, 238
Suint, 425, 438
Sulphatoiodic acid, 363
Sulphalite, 553
Sulphoborite, 430
Sulphohalite, 656
Sulphur, reflecting power-, 222
Superiodides, 233
Sylvine, 15, 430, 522
Sylvinite, 431
Sylvite, 430, 522
Syngenite, 431, 657
Szekso, 710

T

Tachhydrite, 15, 430
Tallingite, 15
Tamarugite, 656
Tartarus vitriolatus, 656
Tellurato-iodic acid, 363
Temperature, effect on equilibria, 145
Tepalcate, 711
Tequezuite, 711
Terlinguaite, 11
Thallic iodate, 355
—— perchlorate, 402
—— periodate, 415
Thallous bromate, 355
—— chlorate, 355
—— iodate, 355
—— perchlorate, 402
—— periodate, 415
Thenardite, 430, 661
Thermochemistry oxychlorine acids, 379
Thermonatrite, 751
Thomsenolite, 1
Thorium bromate, 357
—— chlorate, 357
—— iodate, 354, 357
—— perchlorate, 402
—— periodate, 416
Thulium bromate, 354
Tithonometer, 148
Topaz, 2
Tourmaline, 2
Tri-iodates, 324
Triphane, 425
Triphylite, 426
Trona, 425, 710
Tungstato-periodates, 417
Tungstenato iodic acid, 363
—— periodates, 406
Turner's yellow, 716
Tychite, 656
Tysonite, 1

U

Uranous periodate, 416
Uranyl iodate, 358
—— perchlorate, 403
—— periodate, 416
Uranyl potassium iodate, 358
Urao, 424, 710
Urasite, 656

V

Vanadato iodic acid, 363
Vanadinite, 15
Vanthoffite, 430
Vegetable alkali, 420
Vinasse, 438
Volatile alkalies, 420

W

Weldon mud, 28
White acid, 135
Wool fat, 425, 438

Y

Ytterbium iodate, 355
Yttrium bromate, 354
—— chlorate, 354
—— iodate, 354
—— perchlorate, 402
—— periodate, 415
Yttrocerite, 2

Z

Zinc bromate, 350
—— —— ammino-, 350
—— chlorate, 349
—— —— ammino-, 349
—— hypochlorite, 274
—— iodate, 350
—— —— ammino-, 350
—— perchlorate, 400
—— periodates, 414
Zinnwaldite, 426
Zirconium iodate, 354, 357
Zirconyl bromate, 357
—— chlorate, 357
—— iodate, 357
—— perchlorate, 402
Zootinsalz, 802

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